

**THERMAL, PHOTOCHEMICAL AND ELECTRON-IMPACT  
TRANSFORMATION OF 1,2-DIBENZOYLALKENES AND  
RELATED STUDIES**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
DOCTOR OF PHILOSOPHY

By  
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to the

DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
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## STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

  
S. LAHIRI

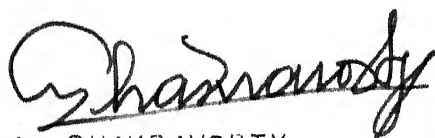
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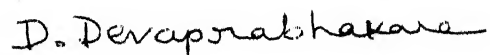
CERTIFICATE I

This is to certify that Miss S. Lahiri has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 501	Advanced Organic Chemistry I
Chm 502	Advanced Organic Chemistry II
Chm 521	Chemical Binding
Chm 523	Chemical Thermodynamics
Chm 524	Modern Physical Methods in Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 581	Basic Biological Chemistry
Chm 611	Organic Reaction Mechanisms
Chm 620	Frontier Topics in Biochemistry and Biophysics
Chm 800	General Seminars
Chm 801	Graduate Seminars
Chm 900	Graduate Research


Miss S. Lahiri successfully completed her Ph.D.  
Qualifying Examination in August, 1973.

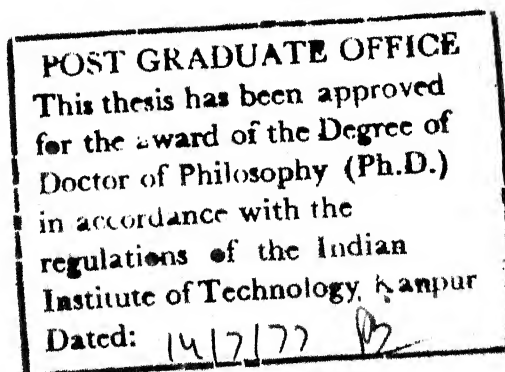
  
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## CERTIFICATE II

Certified that the work embodied in this thesis entitled: "Thermal, Photochemical and Electron-Impact Transformations of 1,2-Dibenzoylalkenes and Related Studies" has been carried out by Miss S. Lahiri under my supervision and the same has not been submitted elsewhere for a degree.

  
M. V. GEORGE  
Thesis Supervisor



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S. LAHIRI

## PREFACE

The thesis entitled: "Thermal, Photochemical and Electron-Impact Transformations of 1,2-Dibenzoylalkenes and Related Studies", is divided into four chapters.

Chapter I deals with the preparation of several cis-1,2-dibenzoylalkenes through the Diels-Alder reaction of different dienes with dibenzoylacetylene. Some of these 1,2-dibenzoylalkenes include, 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (1), 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (2), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (3), 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (4) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (5). The structures of all these adducts have been established through analytical data and spectral evidences. The reaction of cycloheptatriene with dibenzoylacetylene has been examined in detail and was shown to give a mixture of products consisting of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (6) and 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene (7). A reasonable mechanism for the formation of these products has also been suggested. Thermolysis studies of the dibenzoylalkenes, 1-5, have shown that they decompose through a retro-Diels-Alder mode of fragmentation, giving rise to either the diene or the dienophile, in each case. In none

of these cases, the expected pericyclic reaction, analogous to the transformation of cis-1,2-dibenzoylstilbene to the isomeric 2,2,3,4-tetraphenyl-but-3-enolide, has been observed, under thermal conditions. The electron-impact induced transformations of some of these cis-1,2-dibenzoylalkenes (1-6), on the other hand, show that both the retro-Diels-Alder type of fragmentation and pericyclic reaction pathways are followed in these systems.

Chapter II of the thesis deals with the photochemical transformations of some of the cis-1,2-dibenzoylalkenes that we have prepared earlier. Photolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (1), for example, gave a 90% yield of 2,3-dibenzoylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (8), through an intramolecular cycloaddition process. The photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (2), on the other hand, gave a mixture of products consisting of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylic acid (9), 6-(1-phenoxy-1-phenylmethylene)-bicyclo[2.2.2]oct-2-ene-5-endo-carboxylic acid (10) and a lactone, 11, isomeric with the starting material, 2. In the photolysis of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (6), the only product formed was an isomeric lactone, 12, analogous to the formation of 11 in the photolysis of 2. The photochemical transformation of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (3) gave a mixture of products,



consisting of 1,5-dibenzoyl-5-formyl-1,3-cyclopentadiene (13) and dibenzoylacetylene. In the photolysis of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (5), the only product obtained was 1,2-dibenzoyldibenzotricyclo[3.3.0.<sup>2,8</sup>]-octadiene (14), formed through a di- $\pi$ -methane rearrangement. Reasonable mechanisms have been suggested for the formation of the different products in these photochemical reactions.

Chapter III of the thesis describes the preparation of several 1,2-dibenzoylalkenes and related products, formed through the reaction of different nitrogen-containing nucleophiles with dibenzoylacetylene. In the reaction of aniline, piperidine, N-phenylbenzylamine and *o*-aminophenol with dibenzoylacetylene, for example, the corresponding 1:1-adducts, namely, 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (15), 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (16), 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione (17) and 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (18), were formed. The uv-absorption data revealed that the adducts 15 and 18, were the E-isomers, arising through a trans-mode of addition, whereas 16 and 17 were the Z-isomers, formed through a cis-mode of addition.

The reaction of N-phenacylaniline with dibenzoylacetylene gave 2,3-dibenzoyl-1,4-diphenylpyrrole (19),

whereas, in the case of o-phenylenediamine, 2-(2-hydroxy-2-phenyletheno)-3-phenylquinoxaline (20) was formed. Bromination of 20 resulted in the formation of 2-bromophenacyl-3-phenylquinoxaline (21), whereas nickel peroxide oxidation of 20 gave the oxidative dimer, 1,4-diphenyl-2,3-bis(3-phenylquinox-2-yl)butane-1,4-dione (22).

The reaction of 1,8-diaminonaphthalene with dibenzoylacetylene gave a mixture of products consisting of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine (23) and 2-benzoylperimidine (24), whereas in the case of 2-aminopyridine, two 1:1-adducts, namely, 2-(2-imino-1(2H)pyridyl)1,4-diphenylbut-2-ene-1,4-dione (25) and 1,4-diphenyl-2-(N-2-pyridylamino)-but-2-ene-1,4-dione (26) were formed.

Electron-impact induced transformations of the adducts, 15, 16, 17, 18, 19 and 26 revealed that the Z-isomers undergo a different mode of fragmentation, as compared to the E-isomers.

In Chapter IV, the thermal and photochemical transformations of tetraphenyl-p-dioxin (27) and tetraphenyl-p-dithiin (28) are discussed. It has been shown that the thermal rearrangement of tetraphenyl-p-dioxin to 2,2,3,4-tetraphenylbut-3-enolide proceeds through the intermediacy of cis-dibenzoylstilbene. The photolysis of 27, gave a mixture of products consisting mainly of benzil and small amounts of tolan and trans-dibenzoylstilbene. Thermolysis and photolysis of 28, on the other hand, gave tetraphenylthiophene, in each case.

## CHAPTER I

### THERMAL AND ELECTRON-IMPACT INDUCED TRANSFORMATIONS OF *cis*-1,2-DIBENZOYLALKENES

#### I.1 ABSTRACT

Several *cis*-1,2-dibenzoylalkene derivatives have been prepared in yields ranging between 60-80%, through the Diels-Alder addition of the appropriate dienes to dibenzoylacetylene. These include, 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (14), 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (15), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (16), 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20), formed from cyclopentadiene, cyclohexa-1,3-diene, furan, 1,3-diphenylisobenzofuran and anthracene, respectively.

The reaction of cycloheptatriene with dibenzoylacetylene on the other hand, gave a mixture of products consisting of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (22) and 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene (23).

Thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene gave chiefly cyclopentadiene, arising through a retro-Diels-Alder mode of fragmentation. Similar retro-Diels-Alder fragmentations have been observed in the case of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene. The thermolysis of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene, however, gave a mixture of 1,3-diphenylisobenzofuran and 1,2-dibenzoylbenzene. The formation of 1,2-dibenzoylbenzene in this case has been shown to be through the air-oxidation of 1,3-diphenylisobenzofuran. Thermolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene, on the other hand, gave a nearly quantitative yield of 1,2-dibenzoylbenzene, which did not undergo further transformation even on heating around 260° for several hours. In none of these cases, the expected pericyclic transformation, analogous to the conversion of cis-1,2-dibenzoylstilbene (6) to the isomeric 2,2,3,4-tetraphenylbut-3-enolide (9), has been observed under thermal conditions. Treatment of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20) with phosphorous pentasulphide resulted in the formation of a mixture of 12,14-diphenyl-9,10(3',4')furanoanthracene (44) and 12,14-diphenyl-9,10(3',4')thiophenoanthracene (47),

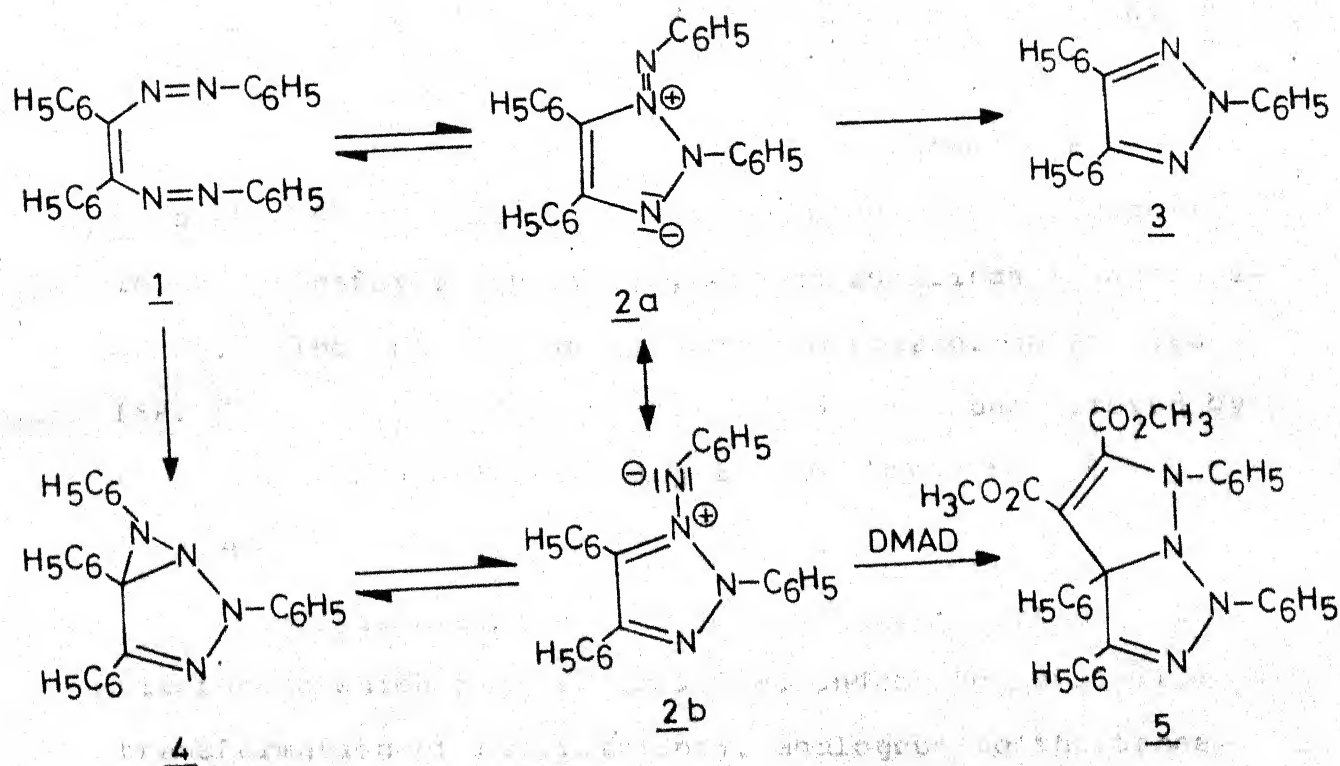
arising through the postulated intermediates, 9,10-dihydro-11-benzoyl-12-thiobenzoyl-9,10-ethenoanthracene (42) and 9,10-dihydro-11,12-dithiobenzoyl-9,10-ethenoanthracene (45), respectively.

The electron-impact induced transformations of the cis-1,2-dibenzoylalkenes, 6, 14, 15, 16, 18, 20 and 22, on the other hand, can be rationalized in terms of both retro-Diels-Alder type fragmentations and pericyclic transformations of the dibenzoylalkene components.

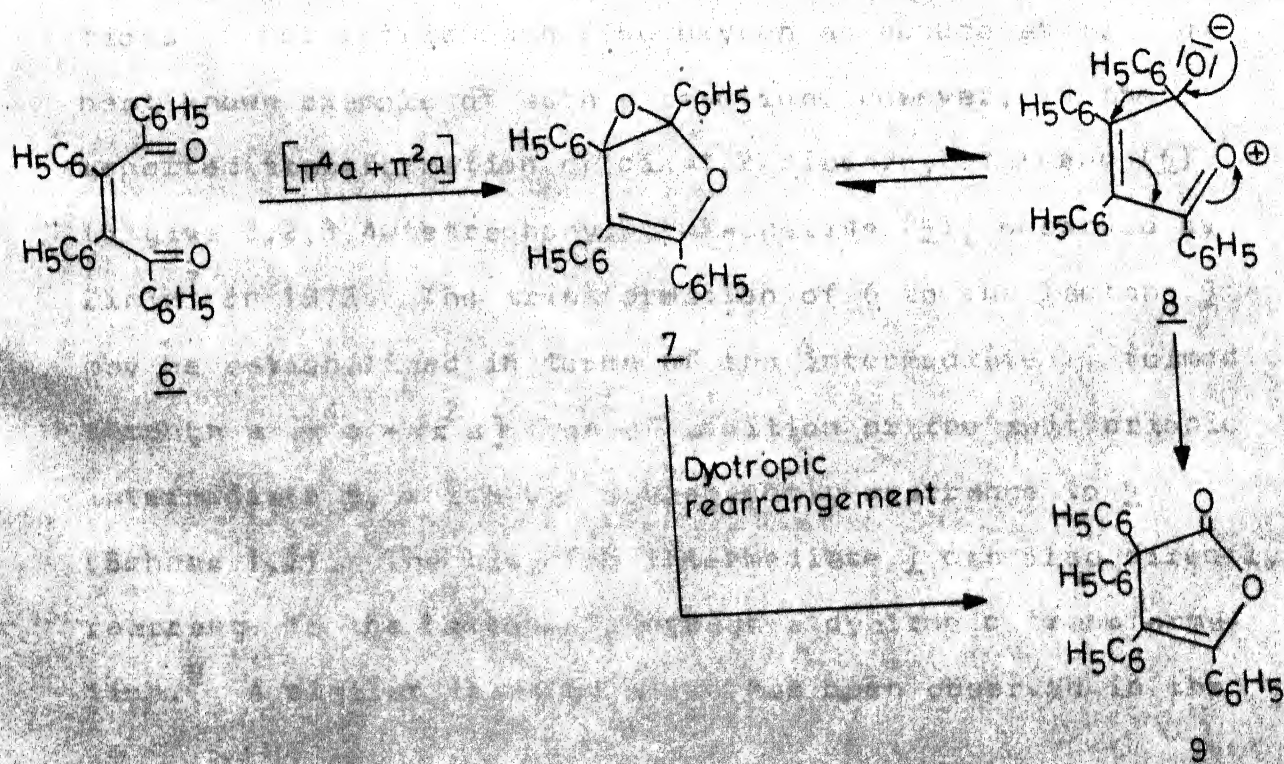
## 1.2 INTRODUCTION

Recent studies have shown that heterotrienenes, in general, can undergo pericyclic transformations leading to the formation of five-membered heterocycles.<sup>1</sup> Thus, it has been observed that the thermolysis of a heterotriene like 1,2-bisphenylazostilbene (1) leads to the formation of 2,4,5-triphenyl-1,2,3-triazole (3) as the major product (Scheme I.1).<sup>2,3</sup> The formation of the triazole 3 in this reaction has been rationalized in terms of the initial pericyclic reaction of 1 leading to the formation of the imino-triazolium intermediate 2, which can subsequently lose phenylnitrene to give 3. The cyclization of 1 to give the intermediate 2 is analogous to the pentadienyl anion cyclizations<sup>4</sup> and will be a symmetry allowed process.<sup>5</sup> An alternative mode of cyclization of 1 would involve a symmetry

### Scheme I.1



### Scheme I.2



allowed  $[\pi^4 a + \pi^2 a]$  type of addition leading to the bicyclic intermediate 4, which can subsequently give rise to the triazole 3, through the loss of phenylnitrene. An example of such a  $[\pi^4 a + \pi^2 a]$  addition has been recently reported in the transformation of 1,2,4-benzoxadiazines to benzoxazoles.<sup>6</sup> The intermediacy of an iminotriazolium species like 2 in the transformation of 1 to 3 has been proved by trapping experiments, leading to the formation of 1,3-dipolar cycloadducts like 5.

Numerous examples of reactions are reported in the literature which can be classified under the pericyclic transformation of heterotrienenes, analogous to the transformation of 1 shown in Scheme I.1. However, a careful survey of the literature has revealed that there are only very few reported examples of such pericyclic transformations of heterotrienenes having oxygen as hetero atom. The best known example of such a reaction, however, is the reported transformation of cis-1,2-dibenzoylstilbene (6) to give 2,2,3,4-tetraphenylbut-3-enolide (9), observed by Zinin<sup>7</sup> in 1872. The transformation of 6 to the lactone 9 may be rationalized in terms of the intermediate 7, formed through a  $[\pi^4 a + \pi^2 a]$  type of addition or the zwitterionic intermediate 8, which can subsequently rearrange to 9 (Scheme I.2). The bicyclic intermediate 7 can also directly rearrange to the lactone 9 through a dyotropic transformation.<sup>8</sup> A similar transformation has been observed in the

thermal conversion of 1,2,4-triphenylbut-2-ene-1,4-dione (32) to 2,2,4-triphenylbut-3-enolide (34)<sup>9</sup> (see, Scheme I.11).

Yet another example of a similar pericyclic reaction involves the thermal rearrangement of symmetrical phthalic bis(tetramethylenedithiocarbamic) anhydride (10) to the unsymmetrical isomer 13, in refluxing benzene.<sup>10</sup> The formation of the unsymmetrical isomer 13 can be rationalized in terms of the pericyclic reaction of 10 to give the zwitterionic intermediate 11, which can undergo transformation to the bicyclo[3.3.1]heptene intermediate 12. Subsequent rearrangement of 12 leads to the formation of 13, as shown in Scheme I.3.

The object of the present investigation has been to examine the possible pericyclic transformations of certain selected examples of cis-1,2-dibenzoylalkene derivatives, under both thermal and electron-impact conditions.

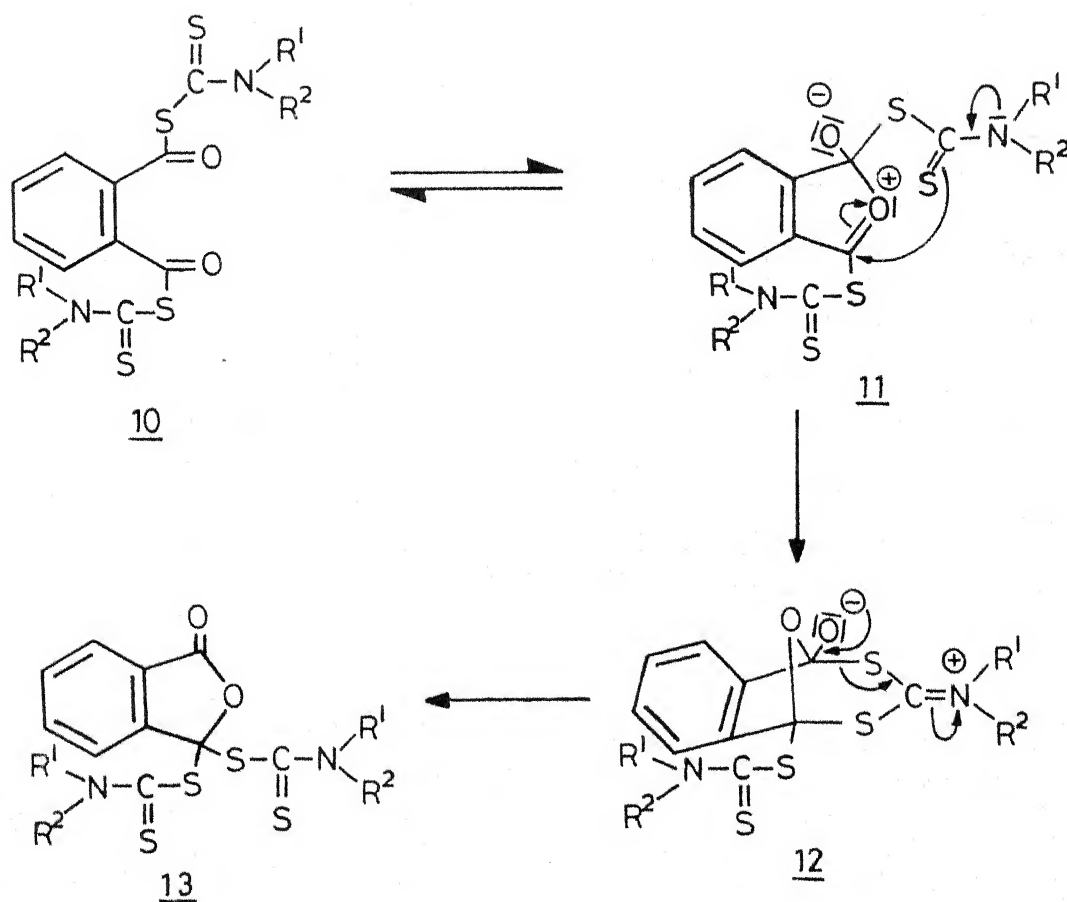
### I.3 RESULTS AND DISCUSSION

#### I.3.1 Synthesis of cis-1,2-Dibenzoylalkenes

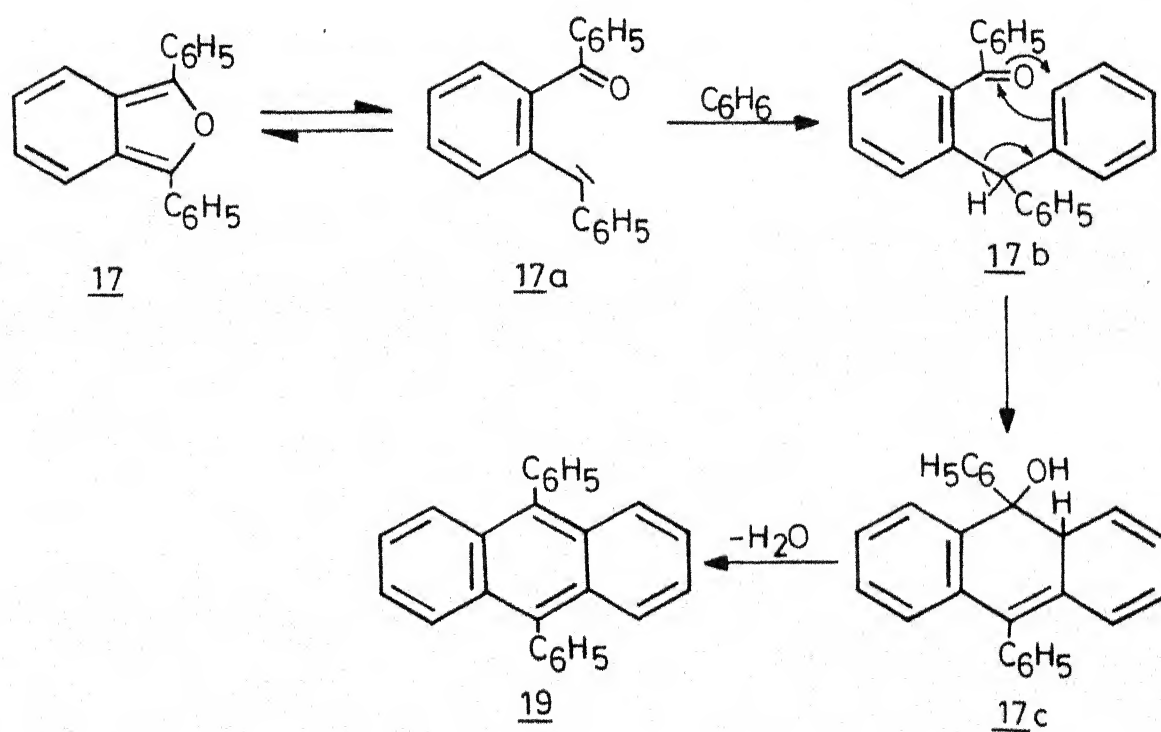
A convenient method of preparing cis-1,2-dibenzoylalkenes would be through the Diels-Alder addition of suitable dienes to dibenzoylacetylene.<sup>11</sup> In our present studies, we have examined the reactions of a few dienes and trienes like cyclopentadiene, cyclohexa-1,3-diene, furan, 1,3-diphenylisobenzofuran, anthracene and cycloheptatriene with dibenzoylacetylene, with a view to preparing



Scheme I.3



Scheme I.4



some cis-1,2-dibenzoylalkene derivatives.

Earlier workers<sup>12-14</sup> have reported the reaction of cyclopentadiene with dibenzoylacetylene to give 2,3-dibenzoyl-bicyclo[2.2.1]hepta-2,5-diene (14). In the present studies we have observed that 14 is formed in a nearly quantitative yield when dibenzoylacetylene is treated with excess of cyclopentadiene at room temperature. The nmr spectrum of 14 (Fig. I.1) is of interest in that it showed two pairs of doublets (AB type of quartet), around 2.32 $\delta$  and 2.65 $\delta$ , assigned to H<sub>a</sub> and H<sub>b</sub> protons, respectively ( $J_{H_a, H_b} = 8$  cps). The doublet around 2.32 $\delta$  due to H<sub>a</sub> proton was further split into a triplet, whereas, the one around 2.65 $\delta$  due to H<sub>b</sub> proton was split into a multiplet. Such a splitting pattern would be expected in view of the fact that the H<sub>a</sub> proton will be split only by the H<sub>c</sub> protons to give the observed triplets ( $J_{H_a, H_c} = 1.5$  cps), whereas, the H<sub>b</sub> proton will be split both by H<sub>c</sub> and H<sub>d</sub> protons, respectively. Similar splitting patterns have been observed in the nmr spectra of certain bicycloheptene derivatives.<sup>15</sup> The two bridgehead protons (H<sub>c</sub>) appeared as a multiplet around 4.27 $\delta$  whereas, the second multiplet around 7.27 $\delta$  has been assigned to the vinylic protons (H<sub>d</sub>). The aromatic protons appeared as a complex multiplet around 7.5 $\delta$  (10 H).

Treatment of a mixture of cyclohexa-1,3-diene and dibenzoylacetylene in refluxing benzene for 8 hr gave a 90%

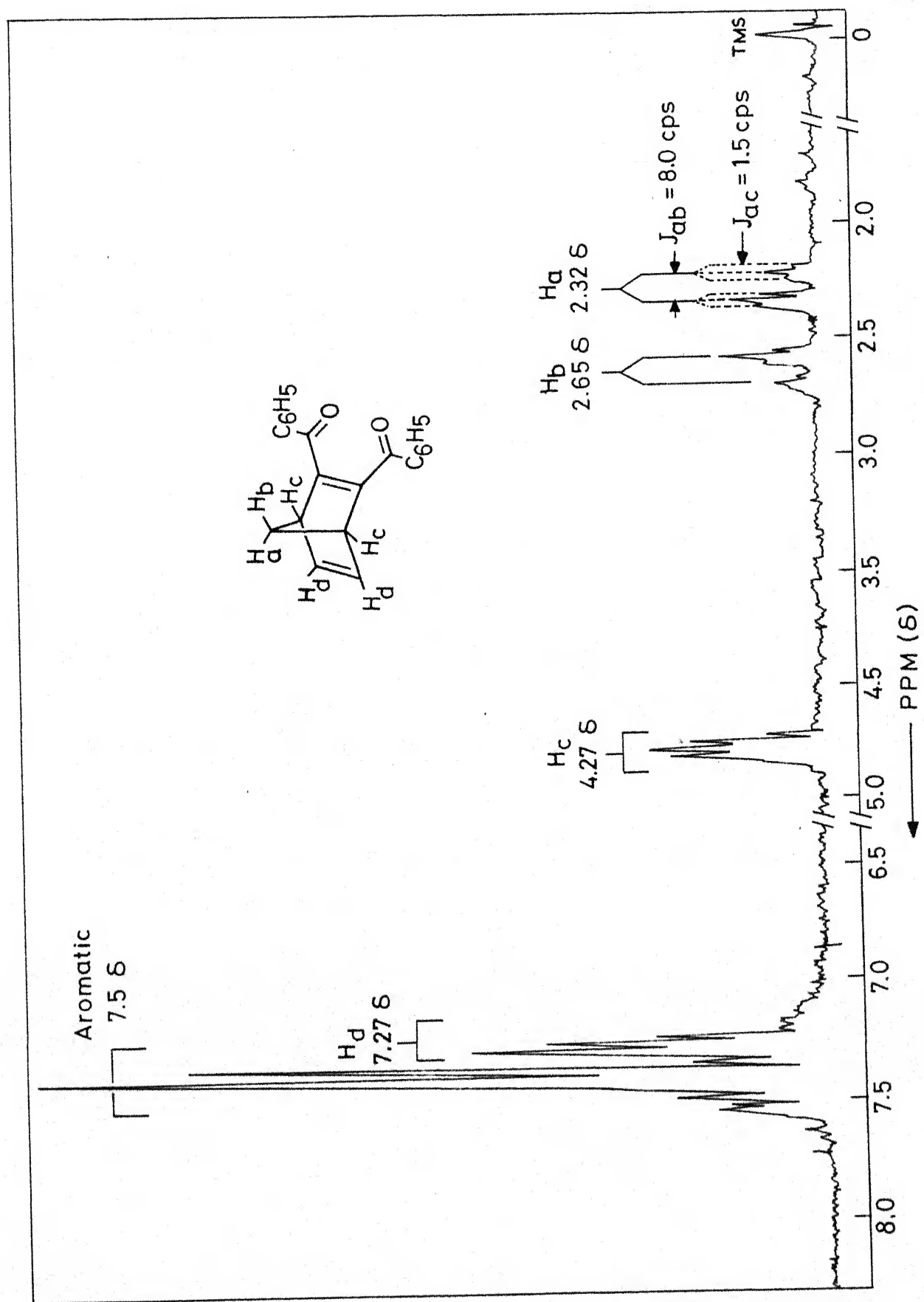


Fig.I.1 NMR spectrum (60MHz) of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (14)

yield of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (15).

The structure of 15 was confirmed on the basis of analytical data and spectral evidences. The nmr spectrum of 15 (Fig. I.2) showed an AB type of quartet and the signals at 1.65 $\delta$  and 1.76 $\delta$  have been assigned to H<sub>a</sub> and H<sub>b</sub> protons, respectively ( $J_{H_a, H_b}$  = 9.5 cps). The multiplet around 4.32 $\delta$  has been assigned to the bridgehead protons (H<sub>c</sub>), whereas the vinylic protons (H<sub>d</sub>) appeared as a multiplet centered around 6.75 $\delta$ . The aromatic protons appeared as a multiplet around 7.45 $\delta$  (10 H).

Neat heating of a mixture of dibenzoylacetylene with excess of furan gave a 77% yield of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (16), identified through analytical data and spectral evidences. The nmr spectrum (Fig. I.3) of 16 showed the bridgehead protons around 6.03 $\delta$  (2H), whereas the vinylic and aromatic protons appeared as a multiplet centered around 7.5 $\delta$  (12 H).

The reaction of 1,3-diphenylisobenzofuran (17) with DBA in refluxing benzene gave a 71% yield of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18). In addition, a 6% yield of 9,10-diphenylanthracene (19) was also isolated from this reaction. The exact mode of formation of 19 in this reaction is not very clear. However, a tentative mechanism for the formation of 19 is shown in Scheme I.4, which essentially involves the reaction of 1,3-diphenylisobenzofuran with benzene. It might be mentioned in this

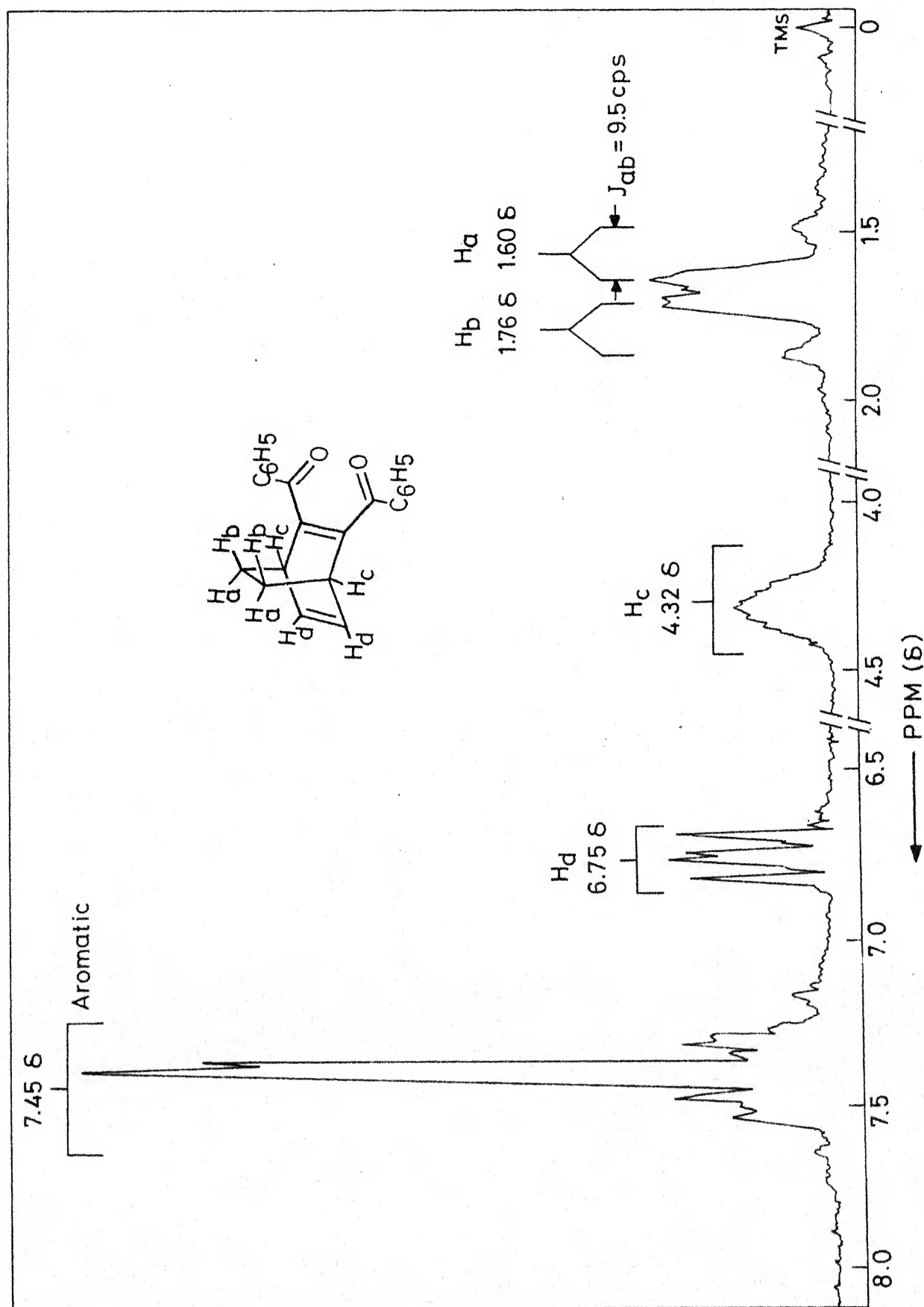


Fig.I. 2 NMR spectrum (60MHz) of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (15)

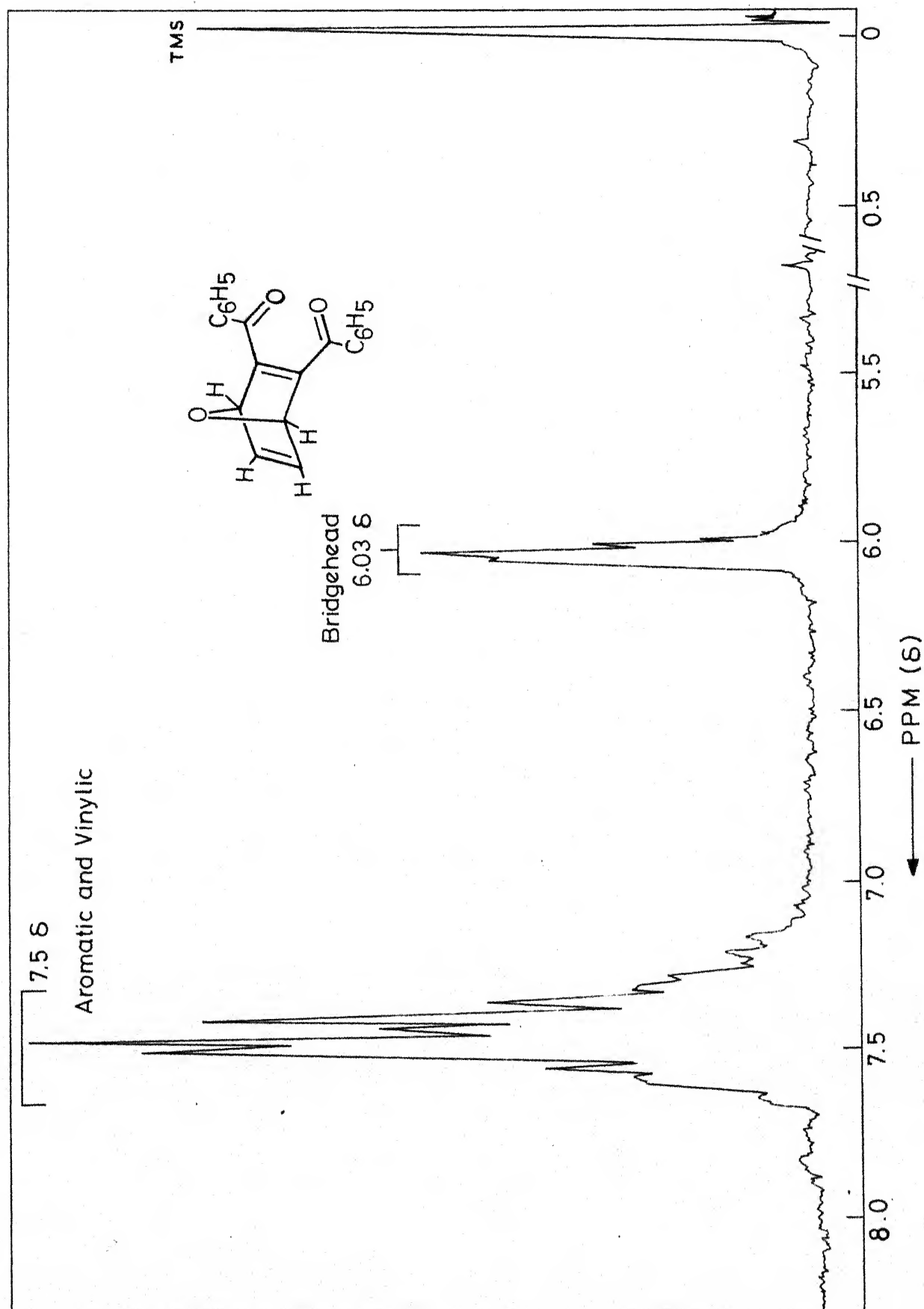


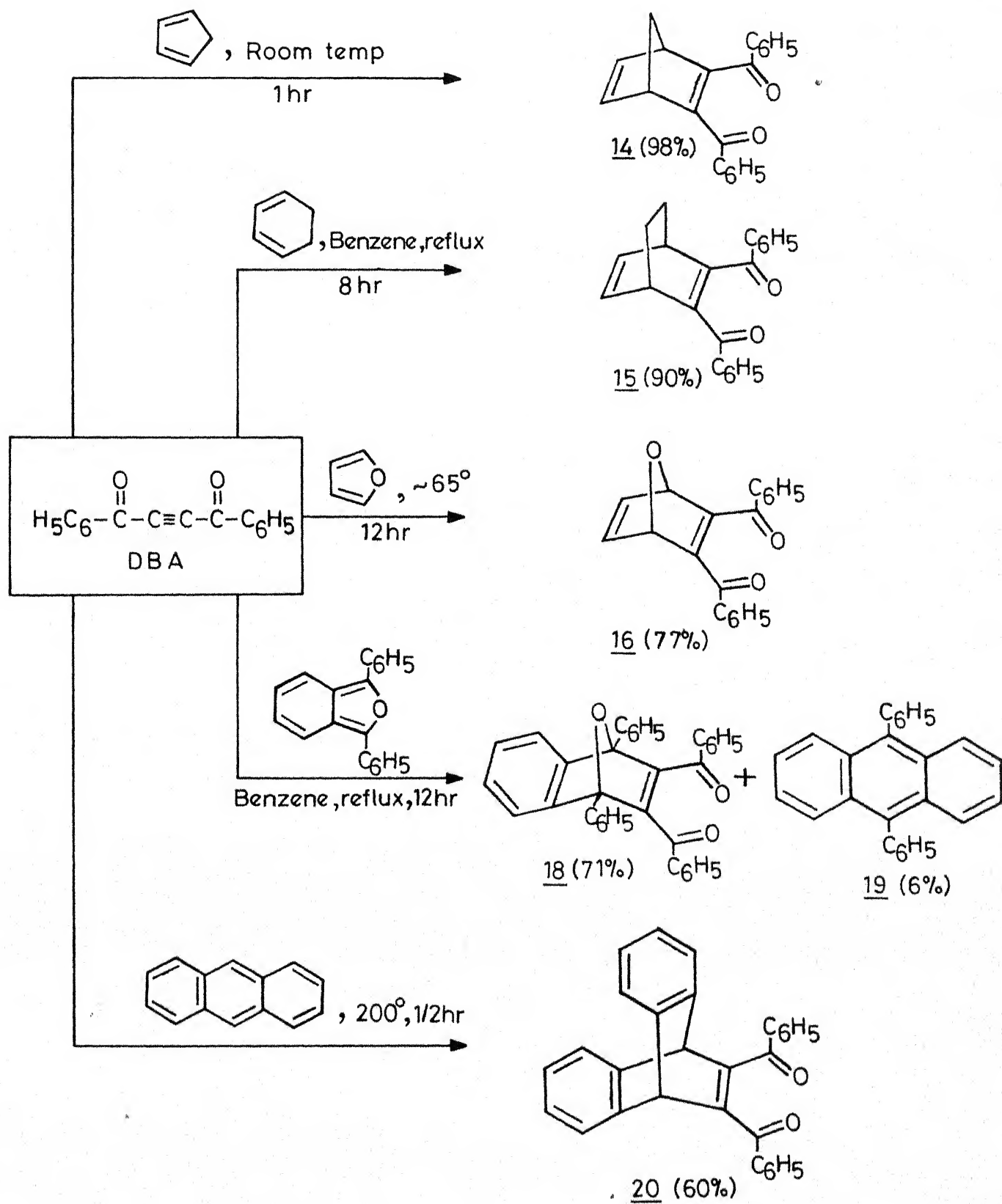
Fig.I. 3 NMR spectrum (60MHz) of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene(16)

connection that the formation of the carbene intermediate 17a, has been postulated in the electron-impact fragmentation of 17.<sup>16</sup> Further support for the pathway shown in Scheme I.4 has been derived from the fact that when 17 alone was refluxed in benzene for 24 hr, 9,10-diphenylanthracene (19) was formed in small amounts (1%), together with 1,2-dibenzoylbenzene.

It has been reported earlier<sup>17</sup> that the reaction of anthracene with DBA gives rise to 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20). We have obtained 20 in a 60% yield by the neat heating of anthracene with DBA around 200° for 30 minutes. Scheme I.5 summarises the results of our studies concerning the preparation of different cis-1,2-dibenzoylalkenes. The structures of these products have been established on the basis of analytical results and spectral data.

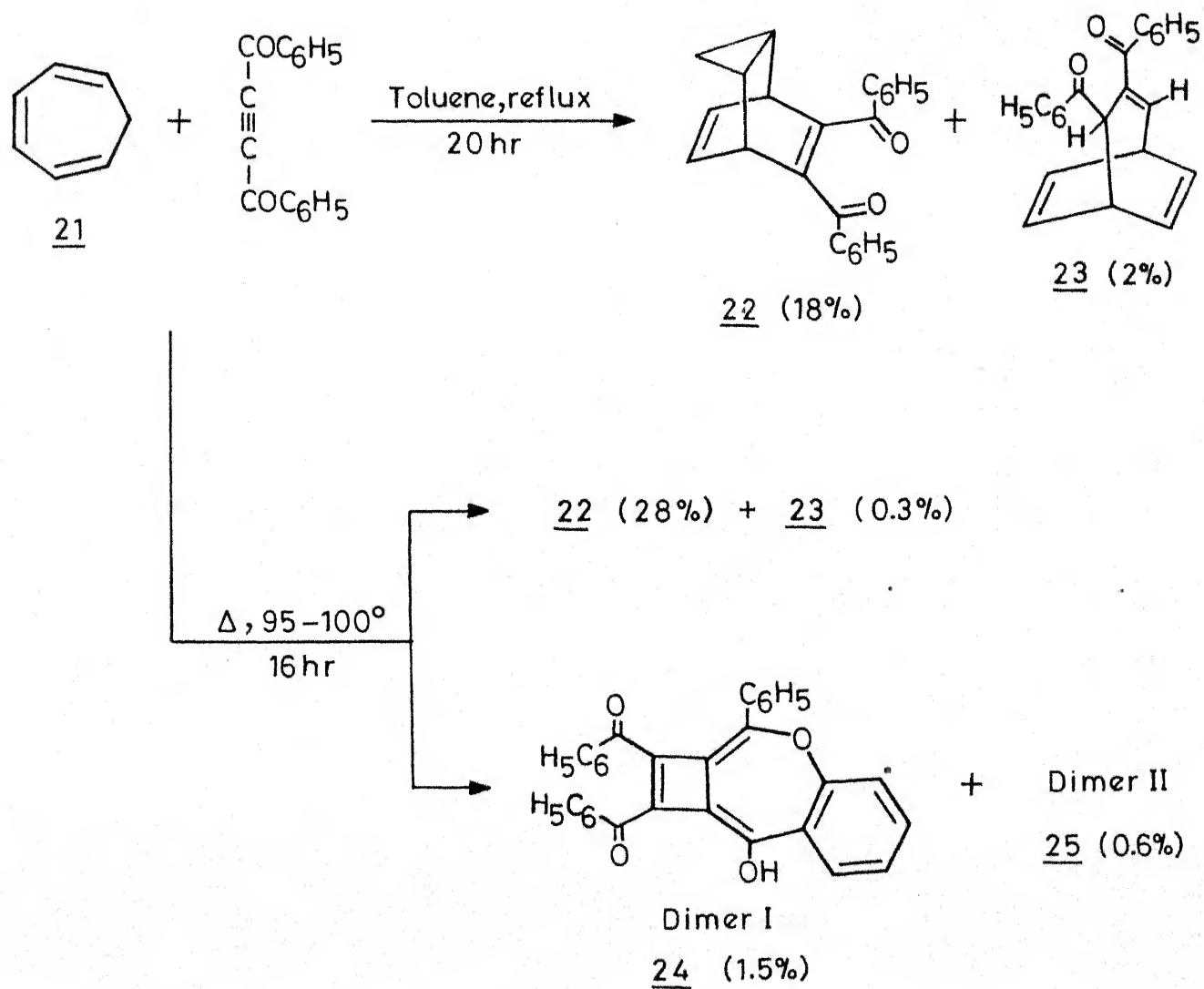
The reaction of cycloheptatriene (21) with DBA deserves special mention. Treatment of a mixture of cycloheptatriene with DBA in refluxing toluene for 20 hr gave a 18% yield of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (22) and 2% of a product, identified as 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene (23) (Scheme I.6). The structure of 22 was confirmed on the basis of analytical results and spectral data. The nmr spectrum of 22 (Fig. I.4), for example, showed several multiplets at 0.72δ (1H), 0.88δ (1H), 1.68δ (2H), 4.30δ (2H), 6.27δ (2H) and 7.22δ (10H). Of these,

Scheme I.5





Scheme I.6



the multiplet at 0.72 $\delta$  has been assigned to the more shielded H<sub>a</sub> proton of the cyclopropane ring. Such shielding effects of the proton endo with respect to the double bond of 22 has been observed in analogous adducts of cycloheptatriene with different dienophiles.<sup>18-20</sup> The signals at 0.88 $\delta$  and 1.68 $\delta$  have been assigned to the H<sub>b</sub> and H<sub>c</sub> protons, respectively, of the cyclopropane ring. The signals at 4.30 $\delta$  and 6.27 $\delta$  have been assigned to the bridgehead and olefinic protons, respectively, whereas the complex multiplet around 7.22 $\delta$  has been attributed to the aromatic protons.

The structure of 23, likewise, has been arrived at, on the basis of spectral evidences and analytical data. The ir spectrum of 23, showed the presence of two carbonyl absorptions at 1680 and 1660 cm<sup>-1</sup>, respectively. It has been observed that in most of the cis-1,2-dibenzoylalkenes that we have examined (Table I.1), the  $\alpha,\beta$ -unsaturated carbonyl absorptions occur around 1635-1660 cm<sup>-1</sup>. On the basis of analogy, therefore, the band at 1660 cm<sup>-1</sup> has been assigned to the  $\alpha,\beta$ -unsaturated carbonyl group in 22, whereas the absorption band at 1680 cm<sup>-1</sup> could be assigned to the carbonyl group, attached to the sp<sup>3</sup> carbon atom.

Further confirmation of the structure of 23 was derived from its uv spectrum. The uv spectrum of 23 showed an absorption maximum at 250 nm, whereas, the dibenzoylalkenes, 14, 15, 16, 18, 20 and 1,2-dibenzoylethylene showed characteristic absorption maxima between 255 and 262 nm. The

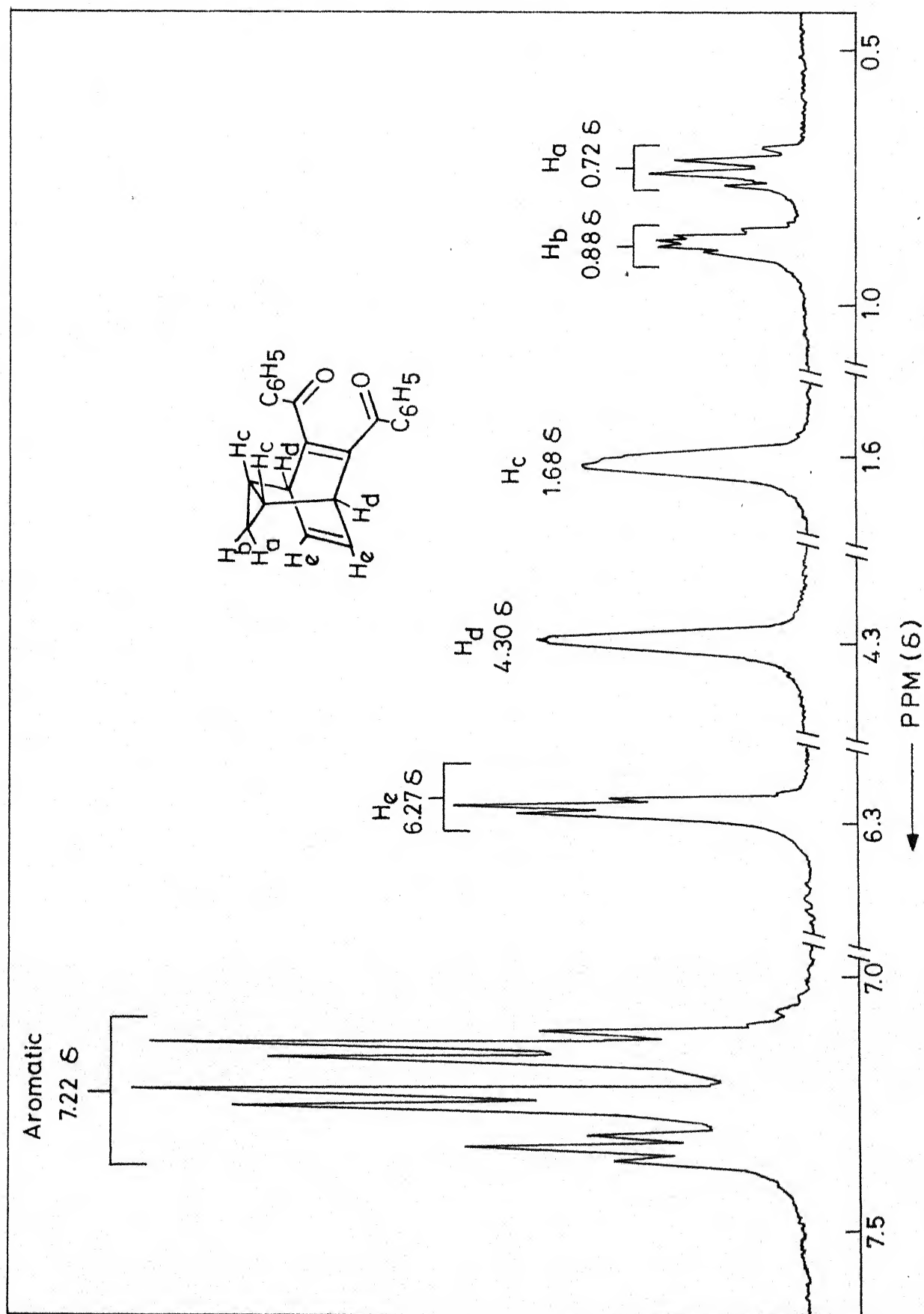


Fig.I. 4 NMR spectrum (270MHz) of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (22)

Table I.1. UV and IR Absorption Characteristics of Some 1,2-Dibenzoylalkenes

Compound	UV absorptions		Ir absorptions	
	$\lambda_{\text{max}}^{\text{EtOH}}$	nm ( $\epsilon$ )	$\nu_{\text{C=O}}, \text{cm}^{-1}$	$\nu_{\text{C=C}}, \text{cm}^{-1}$
1) cis-1,2-Dibenzoylethylene	260	(18,100)	1650	1600, 1580
2) 2,3-Dibenzoylbicyclo- [2.2.1]hepta-2,5-diene ( <u>14</u> )	258	(16,200)	1635	1602, 1575
3) 2,3-Dibenzoylbicyclo- [2.2.2]octa-2,5-diene ( <u>15</u> )	256	(15,100)	1640	1605, 1580
4) 7-Oxa-2,3-dibenzoylbicyclo- [2.2.1]hepta-2,5-diene ( <u>16</u> )	256	(13,000)	1645	1600, 1580
5) 1,4-Diphenyl-2,3-dibenzoyl- 1,4-epoxynaphthalene ( <u>18</u> )	258	(14,000)	1657	1601, 1581
6) 9,10-Dihydro-11,12-diben- zoyl-9,10-ethenoanthracene ( <u>20</u> )	262	(15,000)	1670	1620, 1590
7) 6,7-Dibenzoyltricyclo- [3.2.2.0 <sup>2,4</sup> ]nona-6,8-diene ( <u>22</u> )	255	(13,500)	1645	1595, 1580
8) 3,4-Dibenzoylbicyclo- [3.2.2]nona-2,6,8-triene ( <u>23</u> )	250	(20,000)	1660 and 1680	1600, 1585

absorption maximum in 1,2-dibenzoylethane, however, was observed around 244 nm.<sup>21</sup>

The nmr spectrum of 23 (Fig. I.5) showed a complex multiplet around 3.63 $\delta$  (2H), which may be assigned to the bridgehead protons H<sub>a</sub> and H<sub>b</sub>. The multiplet at 4.88 $\delta$  (1H) may be assigned to the methine proton, H<sub>c</sub>, attached to the carbon atom bearing the benzoyl group. The vinylic proton, H<sub>d</sub>, appeared as a separate multiplet around 6.0 $\delta$ , whereas H<sub>e</sub>, H<sub>f</sub> and H<sub>g</sub> olefinic protons appeared as a complex multiplet around 6.66 $\delta$ . The vinylic proton, H<sub>h</sub>, appeared as a doublet, each one being further split into two separate doublets ( $J_{H_a, H_h} = 8.5$  cps and  $J_{H_c, H_h} = 2$  cps).

Further confirmation of the structure of 23 was derived from its mass spectrum. The mass spectrum of 23 (Fig. I.6) showed a low intensity molecular ion peak at m/e 326 (11%). The most prominent peak in the mass spectrum was observed at m/e 221 and this peak could be assigned to the fragment 23c, formed by the loss of a benzoyl group from 23. Other peaks were observed at m/e 249 (10), 235 (3), 208 (3), 204 (4), 195 (4), 190 (2), 180 (2), 170 (2), 164(2), 157 (12), 144 (24), 130 (8), 126 (4), 116 (12), 114 (8), 105 (83), 92 (19), 91 (33), 77 (42), 65(10) and 51 (24). Some of the fragmentation modes are shown in Scheme I.7. Elimination of a phenyl group from 23, for example, will lead to the formation of 23b at m/e 249. Further loss of a

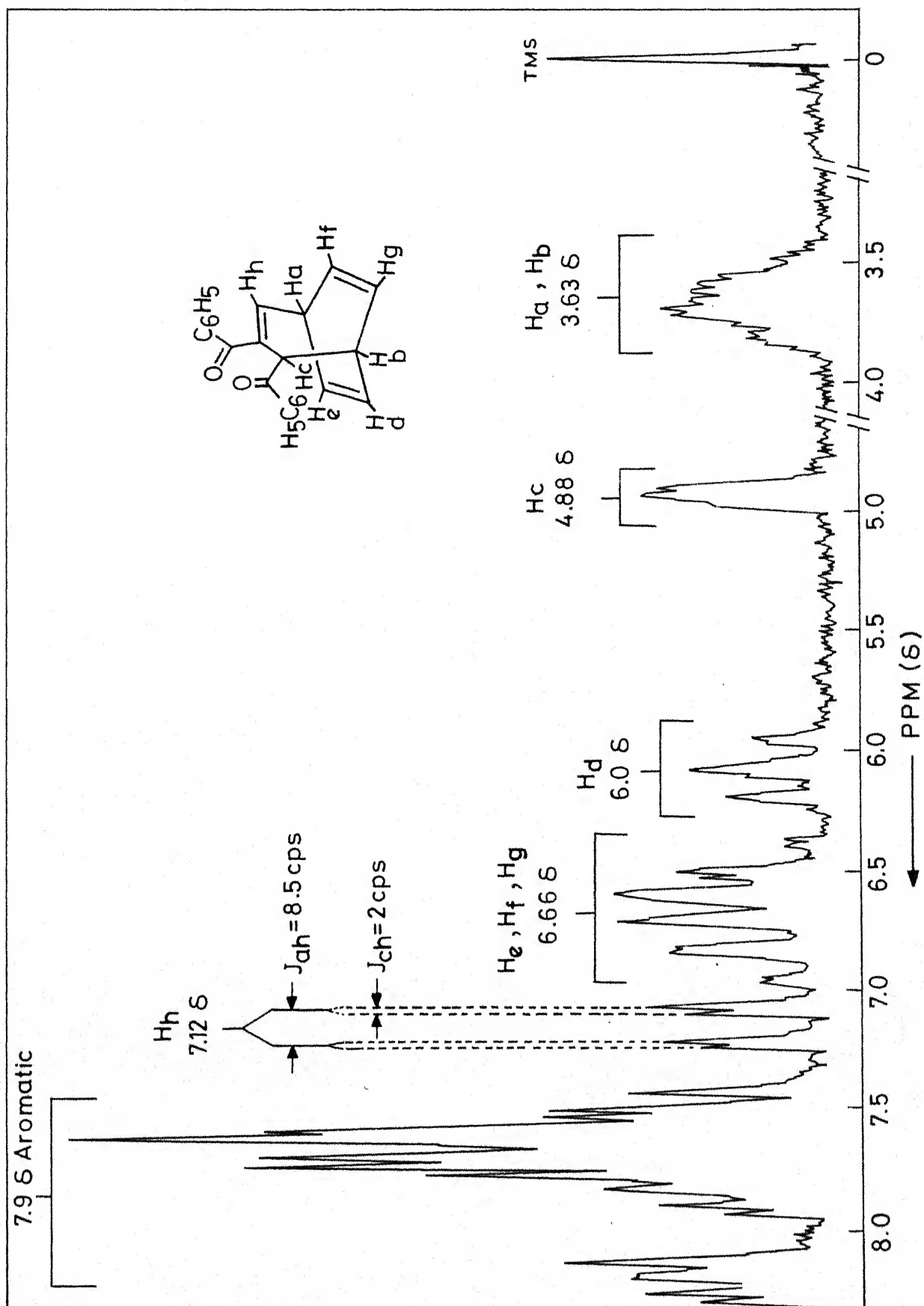


Fig. I. 5 NMR spectrum (60MHz) of 3,4-dibenzoylbicyclo[3.2.2]nona-2,6,8-triene (23)

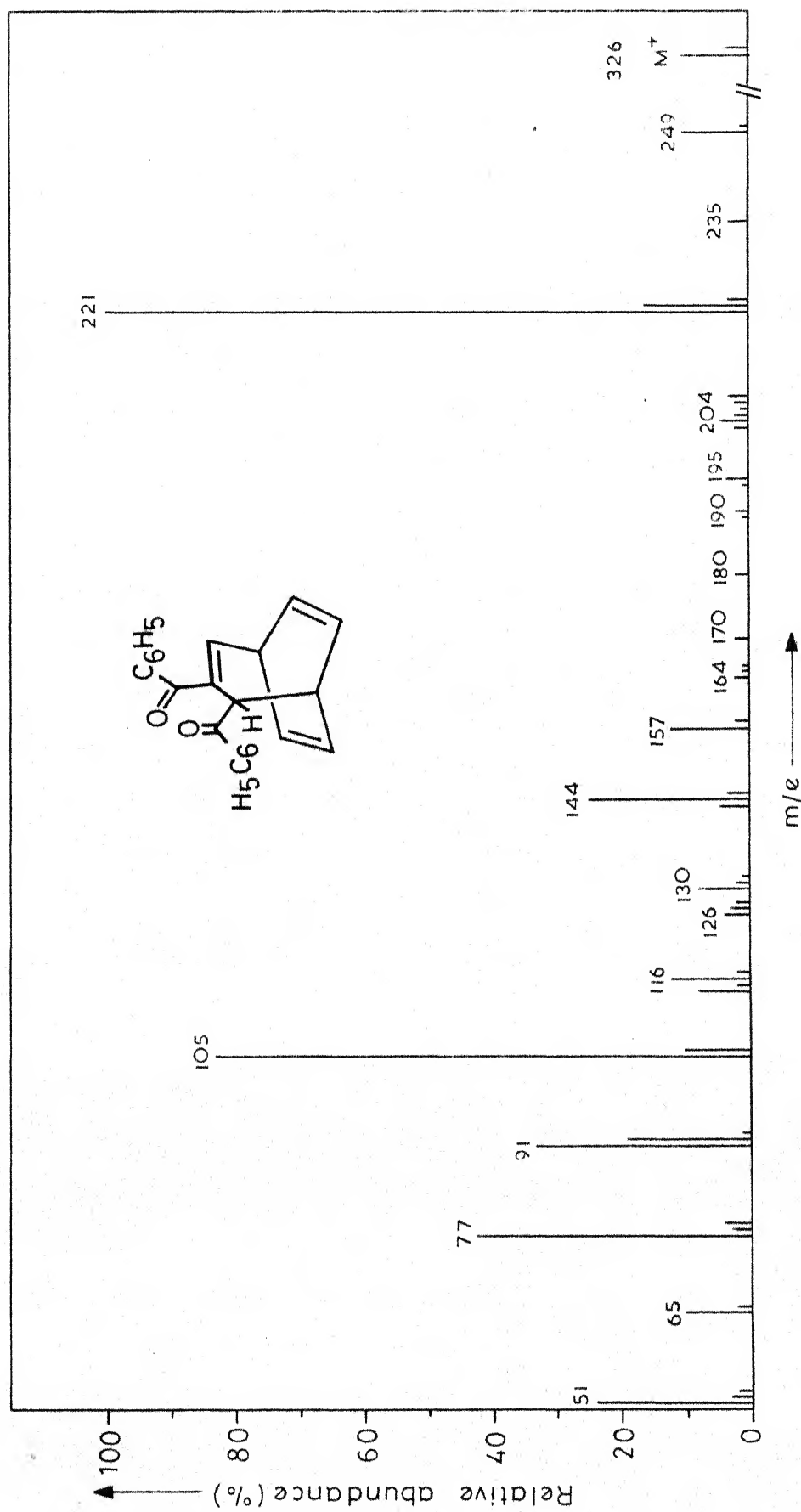
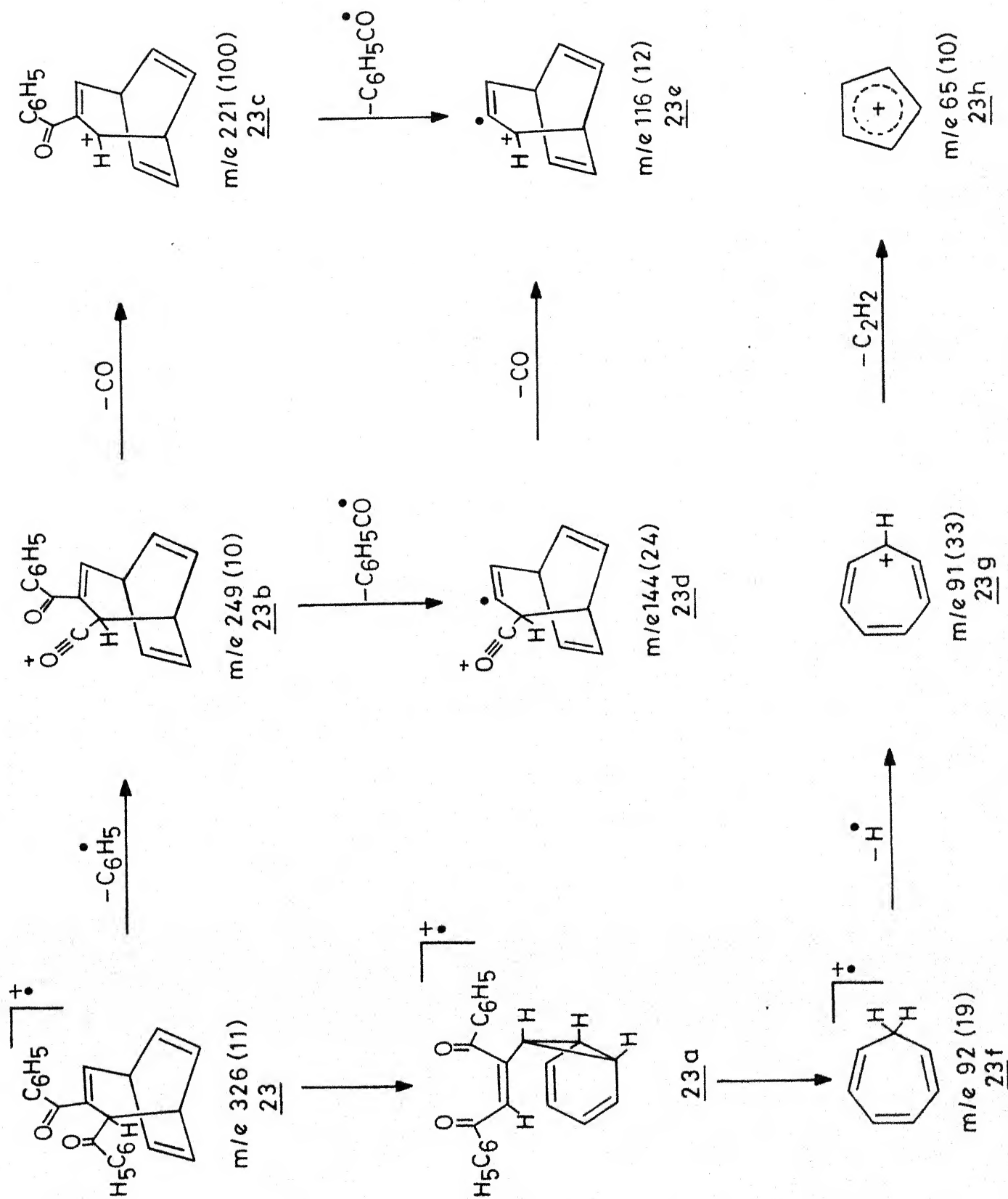


Fig. I. 6 Mass spectrum of 3,4-dibenzoylbicyclo [3.2.2]nona-2,6,8-triene (23)

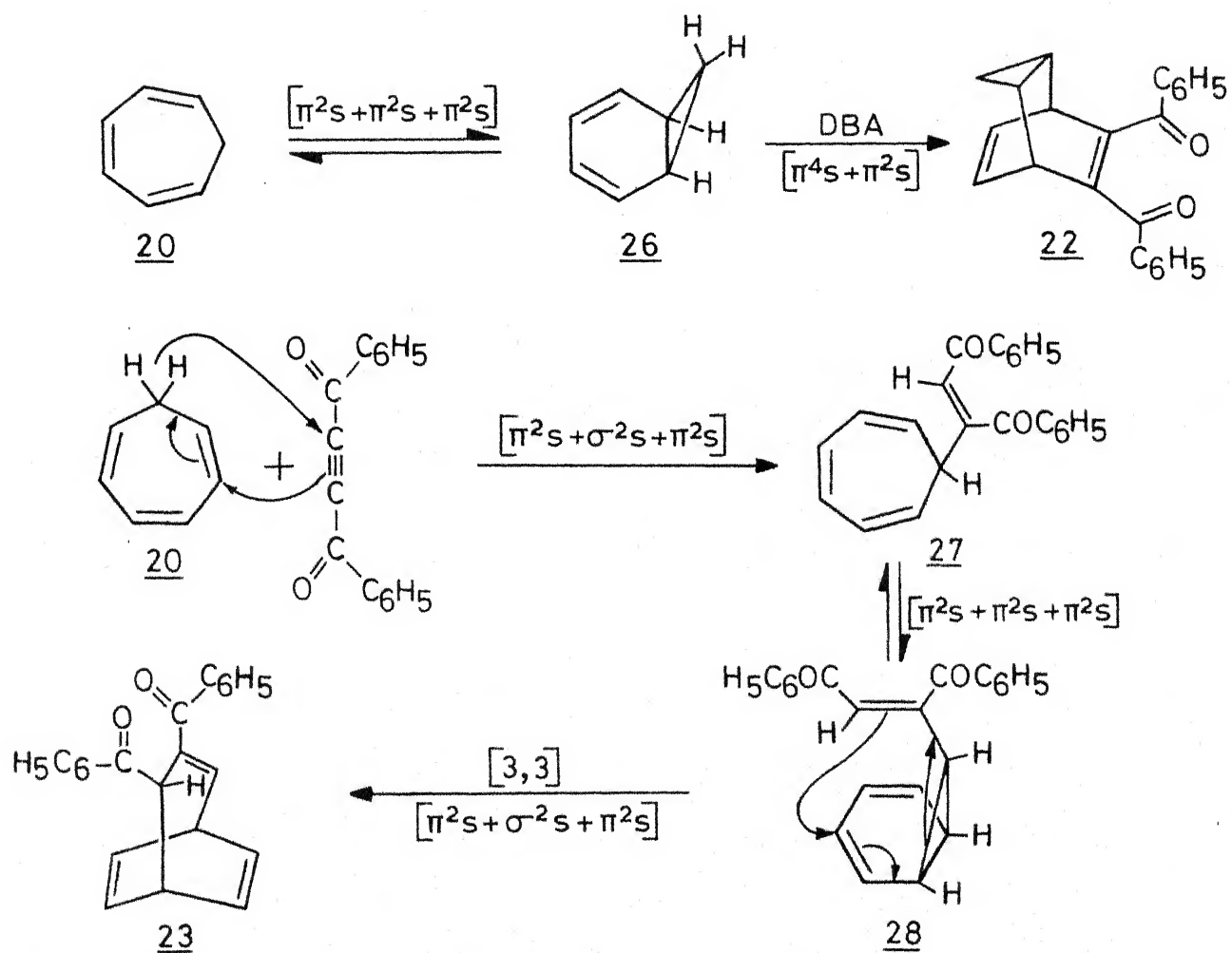
benzoyl group from 23b, will result in the fragment 23d, at m/e 144. A similar loss of one benzoyl group from 23c results in the formation of 23e at m/e 116. A retro-addition mode of fragmentation has been observed due to the presence of the fragment 23i at m/e 235. The peak at m/e 92 can be assigned to the fragment 23f, formed through the fragmentation of 23a, proceeding with hydrogen-transfer. Other peaks in the mass spectrum of 23, can likewise be assigned to some of the fragments shown in Scheme I.7.

The formation of the adducts 22 and 23 in the reaction of cycloheptatriene with DBA has been rationalized in terms of the pathway shown in Scheme I.8. In this scheme we assume that the adduct 22 is formed through the Diels-Alder reaction of the valence isomer 26, of cycloheptatriene (20). Similar addition reactions have been observed in the reaction of cycloheptatriene with dimethyl acetylenedicarboxylate<sup>18,22</sup> and tetracyanoethylene.<sup>20</sup> The formation of the adduct 23, on the other hand, can be rationalized in terms of an initial 'ene-reaction' between cycloheptatriene and DBA to give the intermediate 27, which essentially involves a  $[\pi^2s + \sigma^2s + \pi^2s]$  type of addition reaction. Substituted cycloheptatrienes like 27, bearing ' $\pi$ -acceptor' substituents are known to undergo facile valence isomerization and exist predominantly in the norcaradiene form 28.<sup>23</sup> The norcaradiene intermediate can subsequently undergo a thermally allowed, [3,3] sigma-tropic shift to give the adduct 23 (Scheme I.8). The formation

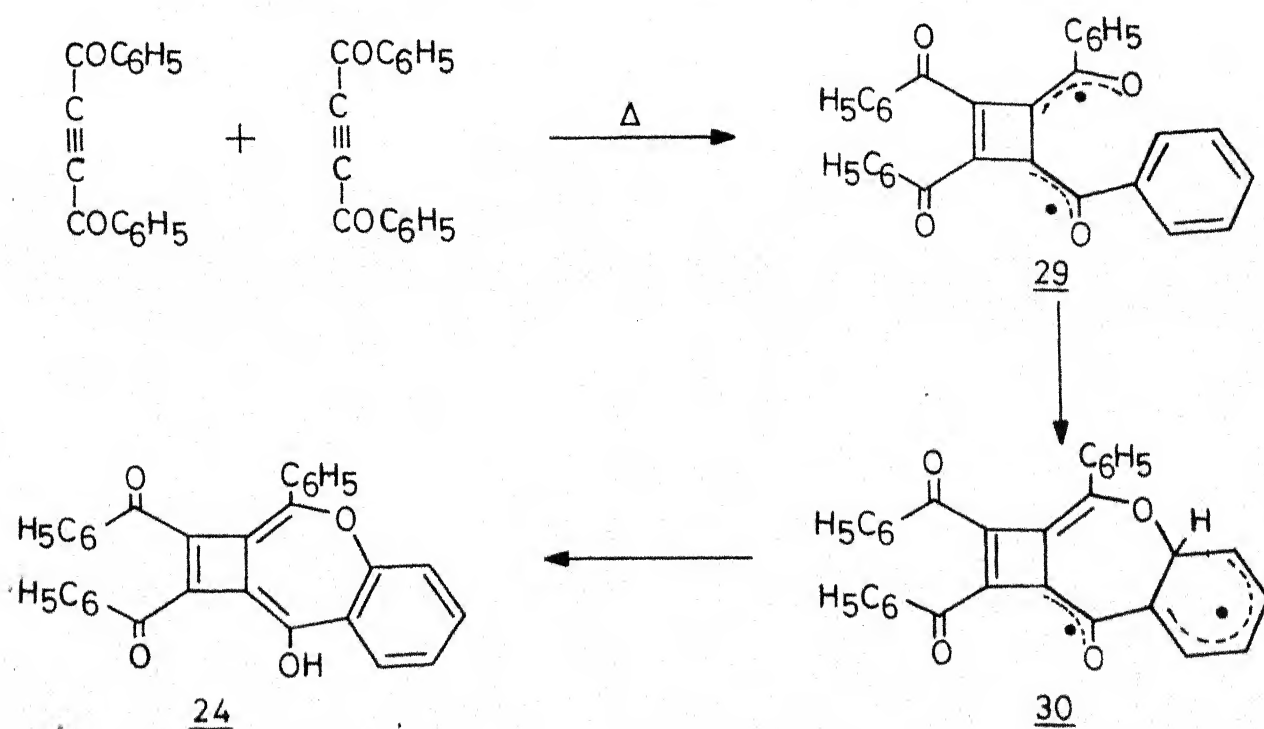








## Scheme I.9



of a similar adduct has been observed earlier in the reaction of cycloheptatriene with dimethyl acetylenedicarboxylate.<sup>22</sup>

When a mixture of DBA and excess of cycloheptatriene (20) was heated around 95-100° for 16 hr, in the absence of any solvent, a 28% yield of 22 and 0.3% yield of 23 were obtained. In addition, small yields of two dimeric products of DBA, tentatively identified as 24 (1.5%) and 25 (0.6%) were also isolated from this reaction. Dimer I, identified as 24, melted at 206° and analysed for  $C_{32}H_{20}O_4$ . The ir spectrum of 24 showed an OH band at  $3455\text{ cm}^{-1}$  and carbonyl absorptions at  $1670$ ,  $1655$  and  $1630\text{ cm}^{-1}$ , respectively. The nmr spectrum of 24 showed a singlet at 4.16 $\delta$  (1H) assigned to the OH proton and multiplets around 7.46 $\delta$  (15H) and 8.26 $\delta$  (4H), assigned to the aromatic protons. Further confirmation of the structure of 24, was derived from its mass spectrum. The mass spectrum of 24 showed a peak at m/e 468, assigned to the molecular ion peak.

The formation of the dimer 24 may be rationalized in terms of the diradical intermediate, 29, formed through a [2+2] addition of DBA as shown in Scheme I.9. The intermediate 29 can subsequently cyclize to give yet another diradical intermediate 30 and further rearrangement of 30, involving hydrogen migration, will lead to the enol 24. Quite recently, Tsutsui et al.<sup>24</sup> have reported the formation of a dimer of DBA, on heating it in decalin or chlorobenzene

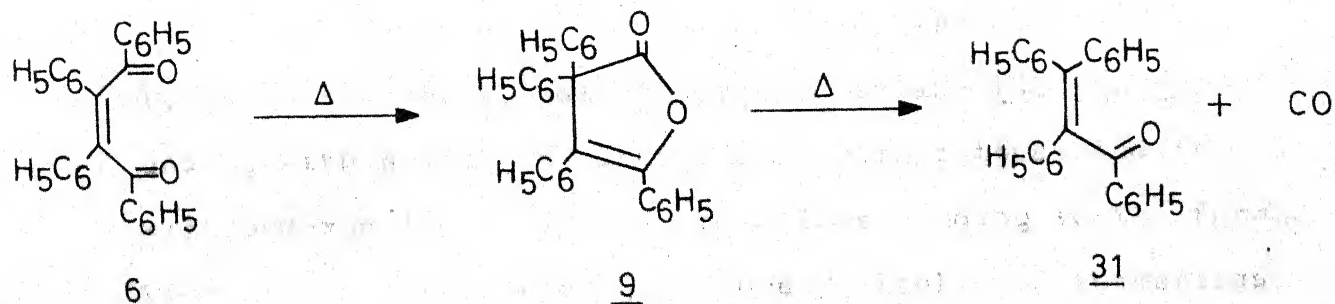
around 150-200° and have assigned the structure 24 for this product.

The dimer II (25), mp 181°, analysed for  $C_{32}H_{20}O_4$ . The mass spectrum of 25 showed a molecular ion peak at  $m/e$  468 and was found to be quite similar to 24, as far as the fragmentation modes are concerned. The exact structure of this dimer has not yet been established.

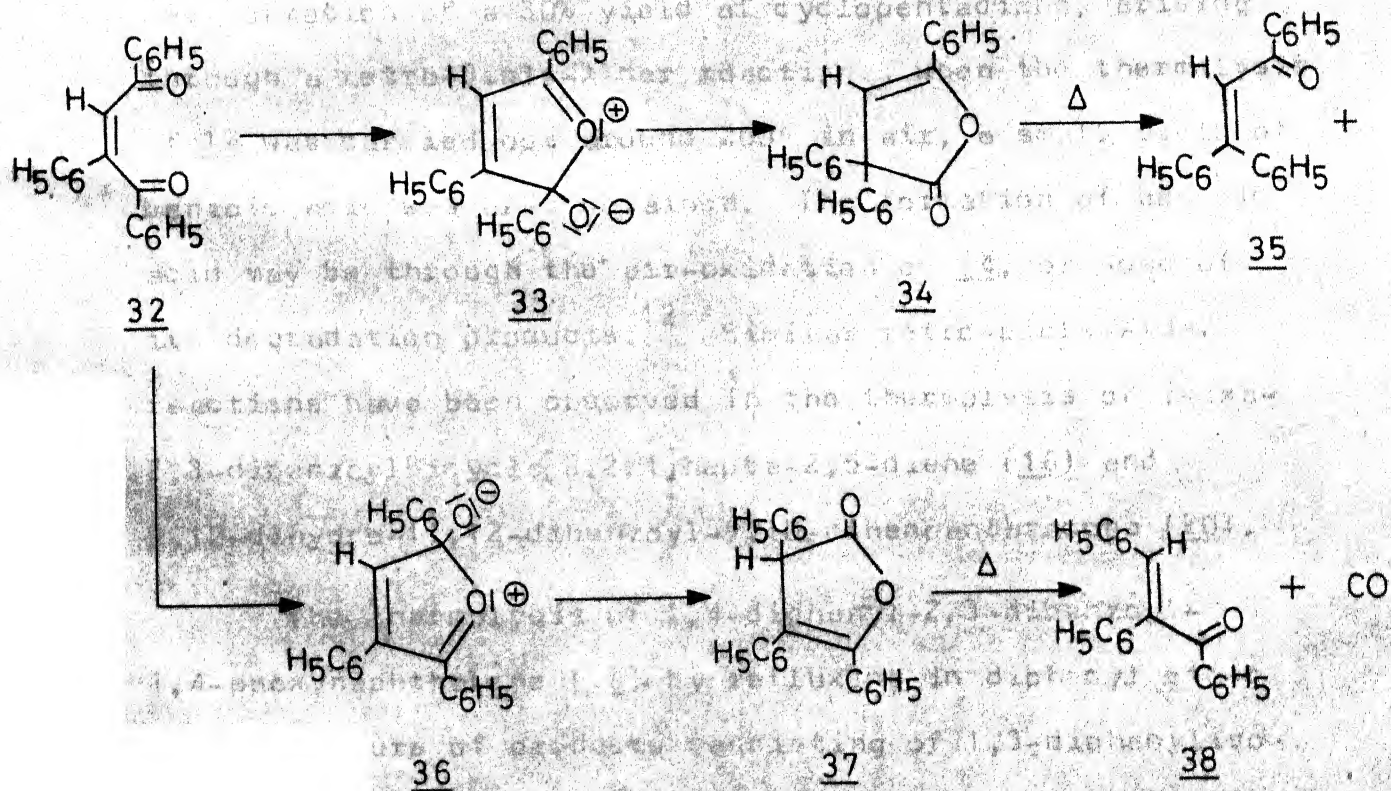
### I.3.2 Thermal Transformations of cis-1,2-Dibenzoylalkenes

It has been reported earlier<sup>7</sup> that on thermolysis, a diketoalkene like cis-1,2-dibenzoylstilbene (6) is quantitatively converted to the lactone 9 at a temperature around 250° (Scheme I.2). At higher temperatures, the lactone 9 itself undergoes decarbonylation to give 1,2,3,3-tetraphenylprop-2-ene-1-one (31), perhaps through a symmetry allowed, linear cheletropic reaction<sup>5,25</sup> (Scheme I.10). It is interesting to note that the thermal transformation of a related 1,2-dibenzoylalkene like 1,2,4-triphenylbut-2-ene-1,4-dione (32) leads to the formation of 2,2,4-triphenylbut-3-enolide (34) and not the isomeric 2,3,4-triphenylbut-3-enolide (37).<sup>9</sup> The structure of 34 was further confirmed through its conversion to the enone 35, on pyrolysis (Scheme I.11). The preferential formation of the lactone 34 in the transformation of 32 may be rationalized in terms of the greater stability of the zwitterionic intermediate 33, when compared

Scheme I.10



Scheme I.11



to the corresponding intermediate 36, in the alternative route which will lead to the lactone 37 (Scheme I.11).

In the present studies we have examined the thermolysis of several 1,2-dibenzoylalkenes like 14, 15, 16, 18 and 20 with a view to finding out whether these substrates will undergo the pericyclic reactions leading to the formation of the corresponding lactones. Table I.2 summarizes the results of our studies. The thermolysis of cis-1,2-dibenzoylstilbene (6) itself was repeated in refluxing nitrobenzene (214°). It was observed that a nearly quantitative yield of the lactone 9 is formed on heating 6, for about 16 hr. The thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (14) around 160°, on the other hand, resulted in the formation of a 30% yield of cyclopentadiene, arising through a retro-Diels-Alder reaction. When the thermolysis of 14 was carried out around 200° in air, a small yield of benzoic acid was also obtained. The formation of benzoic acid may be through the air-oxidation of 14, or some of its degradation products.<sup>12</sup> Similar retro-Diels-Alder reactions have been observed in the thermolysis of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (16) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20).

The thermolysis of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18), by refluxing in diphenyl ether gave a mixture of products consisting of 1,3-diphenylisobenzofuran (17) (2%) and 1,2-dibenzoylbenzene (39) (42%).

Table I.2. Thermal Transformation Products of cis-1,2-Dibenzoylalkenes

Name of the compound	Refluxing solvent	Temp. °C and time	Name of the product	Yield (%)
cis-1,2-Dibenzoylstilbene ( <u>6</u> )	Nitrobenzene	214°; 20 hr	2,2,3,4-Tetraphenylbut-3-enolide ( <u>9</u> )	96%
2,3-Dibenzoylbicyclo[2.2.1]-hepta-2,5-diene ( <u>14</u> )	Neat	160°; 4 hr	Cyclopentadiene	63%
2,3-Dibenzoylbicyclo[2.2.2]-octa-2,5-diene ( <u>15</u> )	Neat	160°; 2 hr	1,2-Dibenzoylbenzene ( <u>39</u> )	99%
7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene ( <u>16</u> )	Dioxan	100°; 4 hr	Dibenzoylacetylene	91%
1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene ( <u>18</u> )	Diphenyl-ether	210°; 12 hr	1,3-Diphenylisobenzofuran + 1,2-Dibenzoylbenzene ( <u>39</u> )	2% 42%
9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene ( <u>20</u> )	Neat	260°; 2 hr	Anthracene	83%

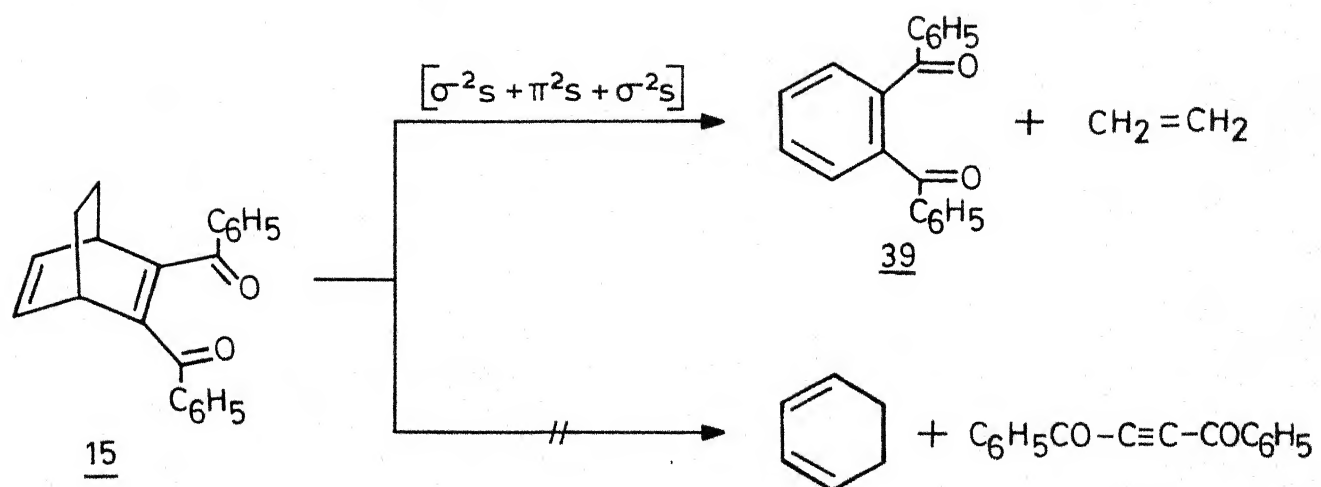


The formation of 39 in this reaction is assumed to be through the air-oxidation of 1,3-diphenylisobenzofuran.<sup>26,27</sup> In a separate experiment we have shown that by refluxing 1,3-diphenylisobenzofuran alone in diphenyl ether for 18 hr, a 73% yield of 39 is formed.

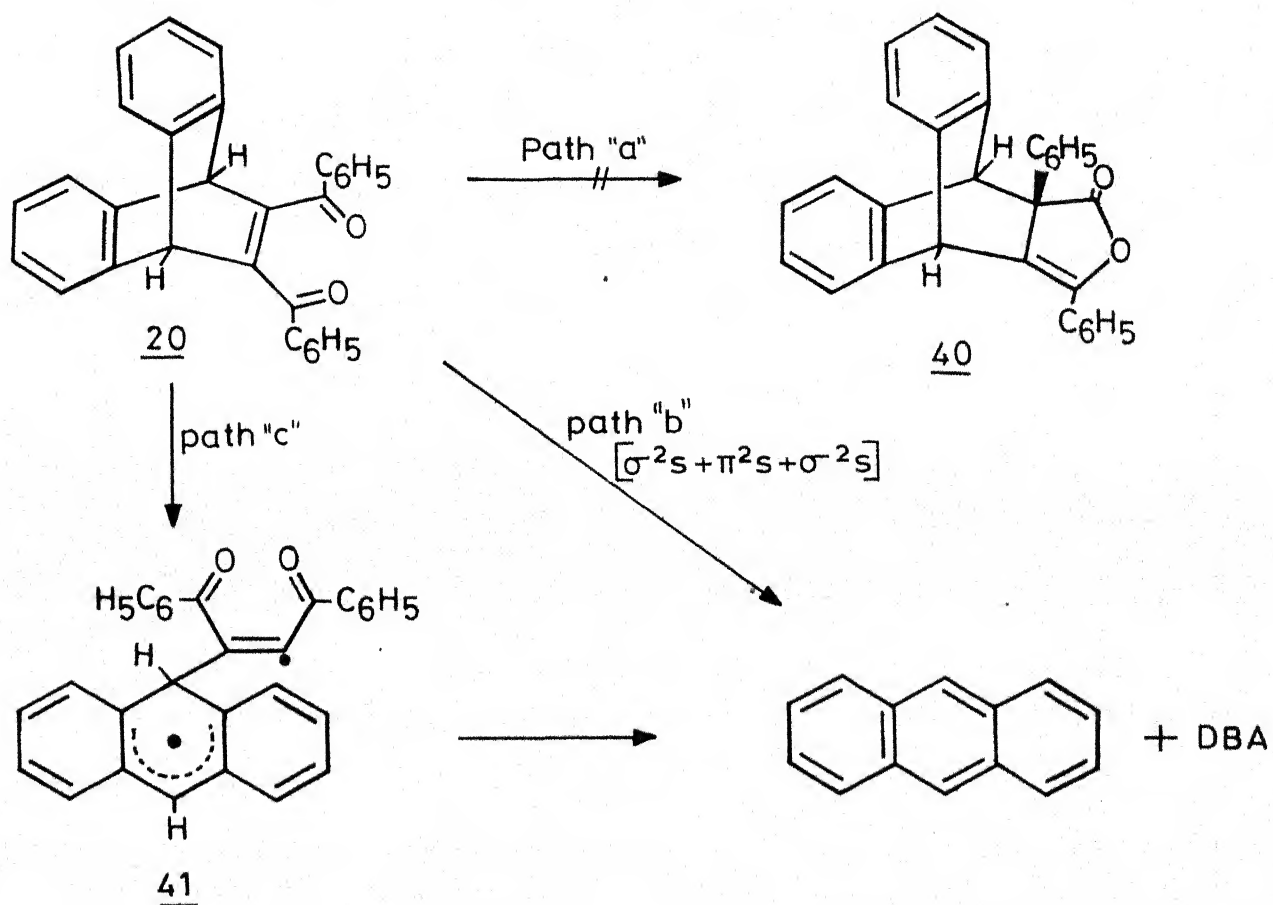
The thermolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (15) is of interest in that, it gives rise to a nearly quantitative yield of 1,2-dibenzoylbenzene (39). It is apparent that the loss of ethylene through a symmetry allowed  $[\sigma^2s + \pi^2s + \sigma^2s]$  process is more favoured than a simple retro-Diels-Alder fragmentation leading to the formation of 1,3-cyclohexadiene (Scheme I.12).

Our studies involving the thermal transformations of cis-1,2-dibenzoylalkenes like 14, 16, 18 and 20 clearly indicate that in these cases the retro-Diels-Alder mode of fragmentation is preferred over the pericyclic transformation. Thus, in the thermal decomposition of 20, it appears that the energetically favourable pathway is the formation of anthracene and not path 'a' leading to the formation of the lactone 40 (Scheme I.13). However, it is not very clear whether the retro-Diels-Alder reaction leading to the formation of anthracene is proceeding through a symmetry allowed,  $[\sigma^2s + \pi^2s + \sigma^2s]$  mode (path 'b') or through a multistep pathway, involving the diradical intermediate 41 (path 'c').

Scheme I.12



Scheme I.13

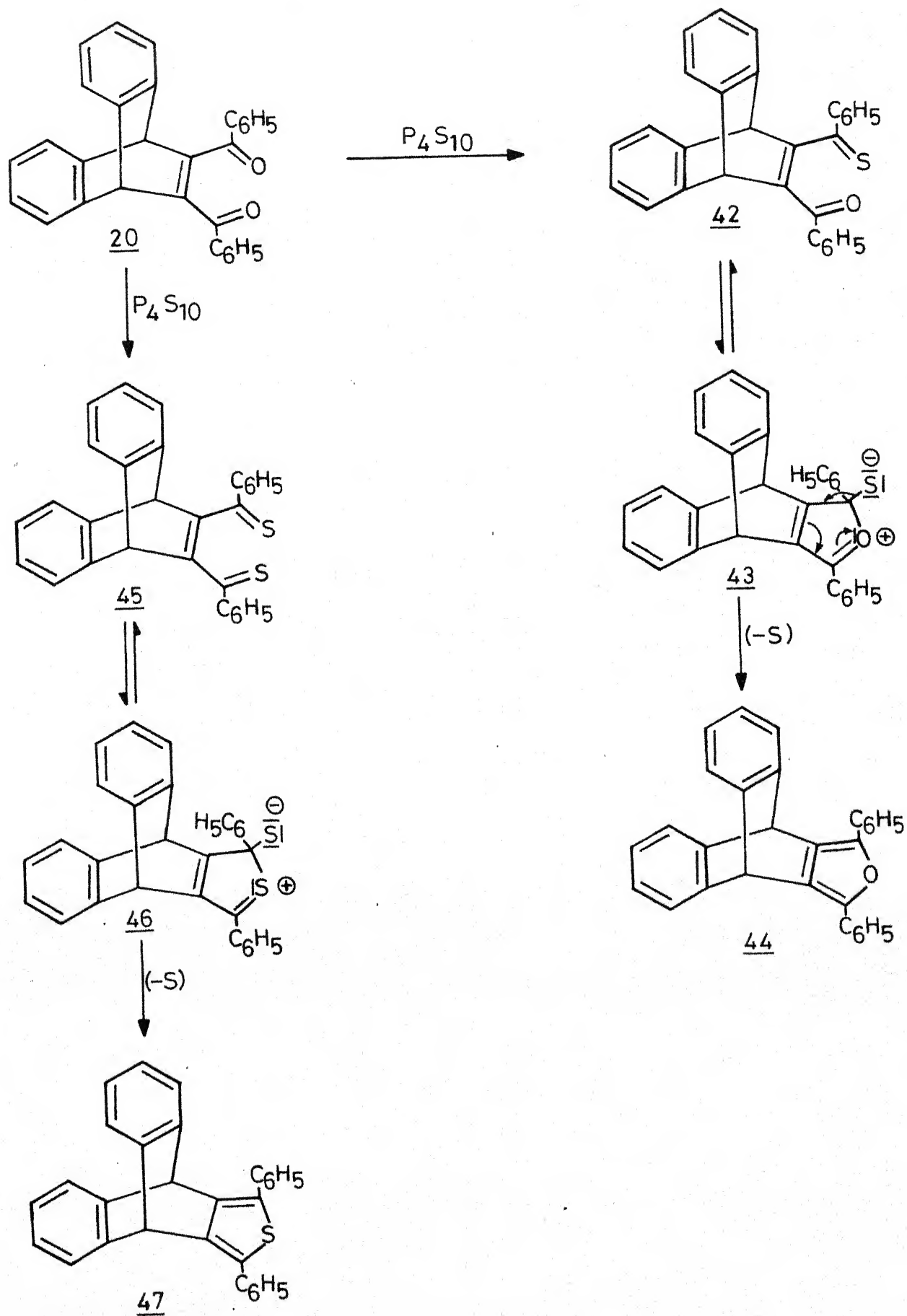


We reasoned that the pericyclic transformation of a heterotriene like 20, proceeding through path 'a', may be more favoured if the hetero atoms are changed from oxygen to sulphur, as in the case of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (45). With this view in mind, we have examined the reaction of 20 with phosphorous pentasulphide. Treatment of 20 with phosphorous pentasulphide in refluxing xylene for 1 hr gave a mixture of 12,14-diphenyl-9,10(3',4')-furanoanthracene (44) and 12,14-diphenyl-9,10(3',4')thiophenoanthracene (47), from which 25% yield of pure 44 could be isolated through adduct formation with maleic anhydride.

The structure of 44 was confirmed on the basis of analytical results and spectral data. The mass spectrum of 44 (Fig. I.7), for example, showed a molecular ion peak at  $m/e$  396(100). Other peaks in the spectrum were observed at  $m/e$  319(3), 318(4), 317(3), 292(9), 291(35), 290(13), 289(34), 288(5), 287(9), 188(7), 178(7), 159(4), 145(3), 144(2), 105(62), 77(80) and 51(8). Some of these fragmentation modes are shown in Scheme I.15.

The mass spectrum of the mixture consisting of 44 and 47, on the other hand, showed prominent peaks at  $m/e$  412(100) and  $m/e$  396 (51), corresponding to their molecular ions. Our attempts to isolate a pure sample of 47 from this mixture have been unsuccessful.

Scheme 1.14



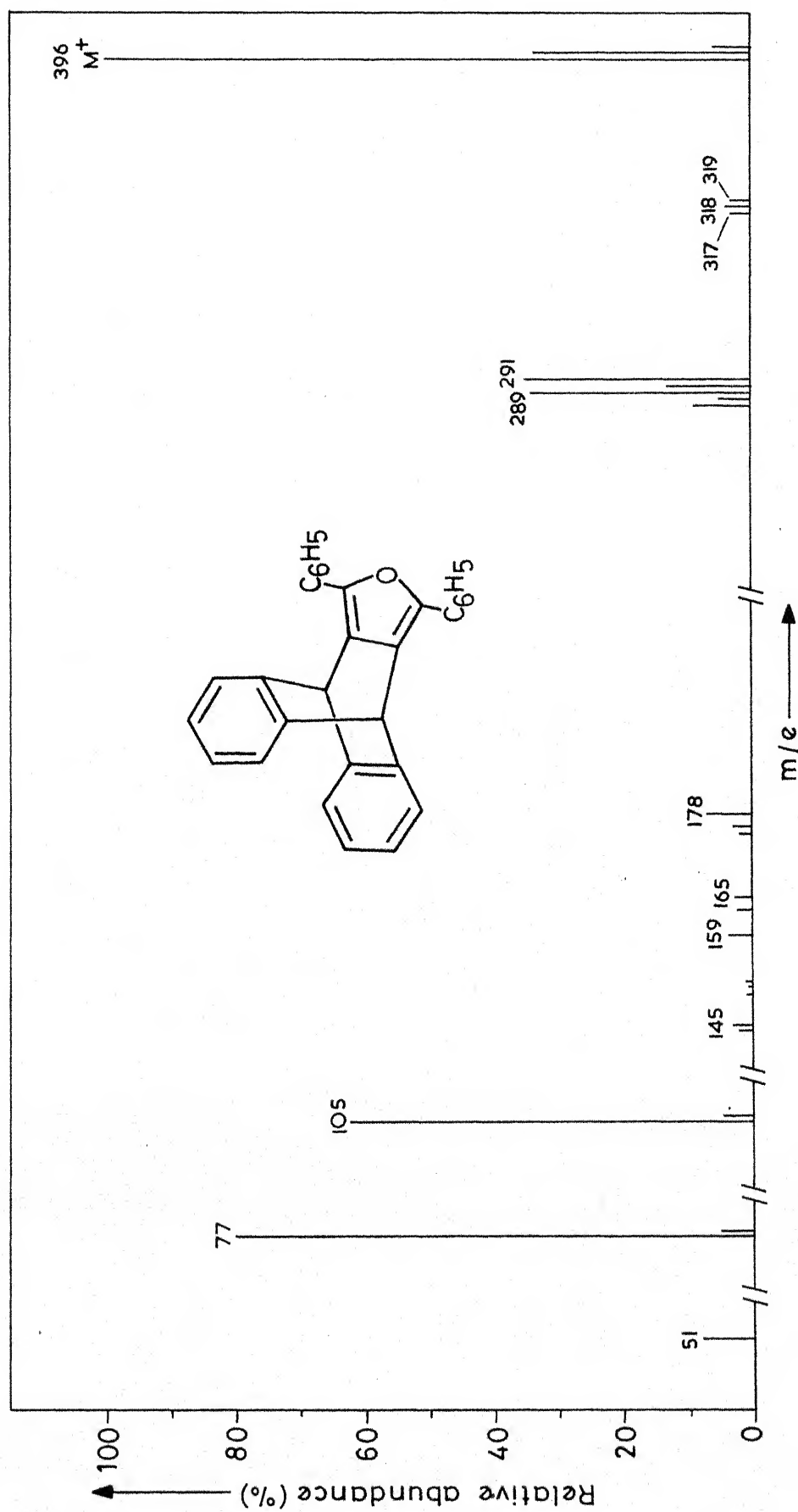
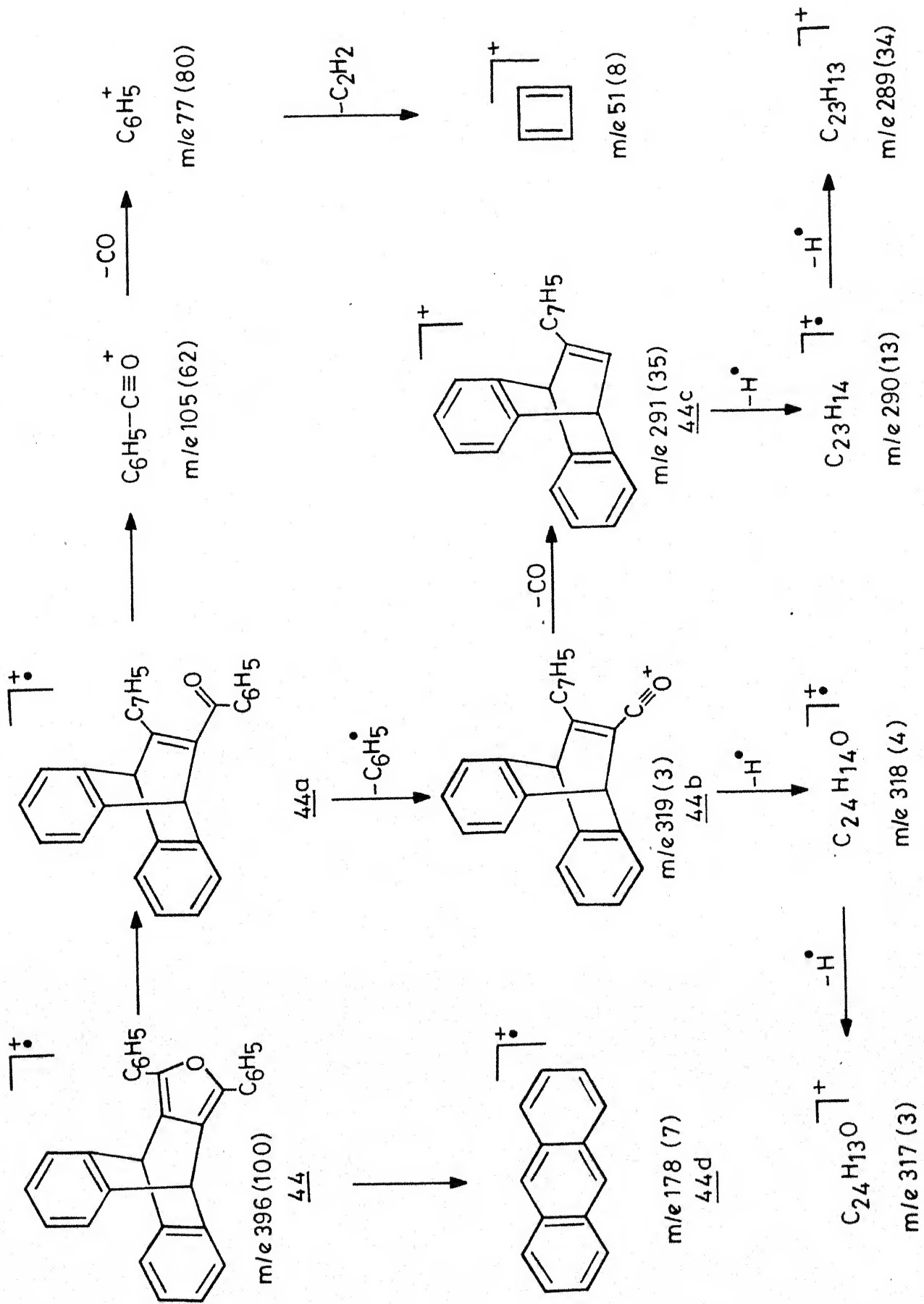


Fig.I.7 Mass spectrum of 12,14-diphenyl-9,10 (3',4') furanoanthracene (44)



### I.3.3 Electron Impact Transformation of cis-1,2-Dibenzoyl-alkenes

In contrast to the numerous studies on the mass spectral fragmentations of saturated aliphatic ketones, only scant attention has been paid to the study of unsaturated ketones.<sup>28-34</sup> Djerassi and coworkers<sup>31</sup> for example, have studied the mass spectral fragmentations of several aryl and alkyl substituted  $\Delta^2$ -cyclohexenones and related bicyclic ketones and have shown that decarbonylations, followed by known skeletal rearrangements are occurring in these systems.<sup>35,36</sup> No detailed study has so far been made on the mass spectral fragmentations of 1,4-dicarbonylalkenes or related systems. In the present investigation we have examined the mass spectral fragmentations of a few representative cis-1,2-dibenzoylalkenes with a view to studying the mode of cleavage in these systems and also to compare their electron-induced and thermal modes of transformations.

The mass spectrum of cis-1,2-dibenzoylstilbene (6) (Fig. I.8), for example, showed the molecular ion peak at m/e 388 (28). Other peaks were observed at m/e 283 (26), 255 (26), 178 (60), 105 (100) and 77 (98) which could be assigned to some of the fragments shown in Scheme I.16. The peak at m/e 372 could be assigned to the fragment 6b, formed through the loss of oxygen from the intermediate 6a. Further loss of a benzoyl fragment from 6b could lead to the formation of the fragment 6d at m/e 267. Another mode

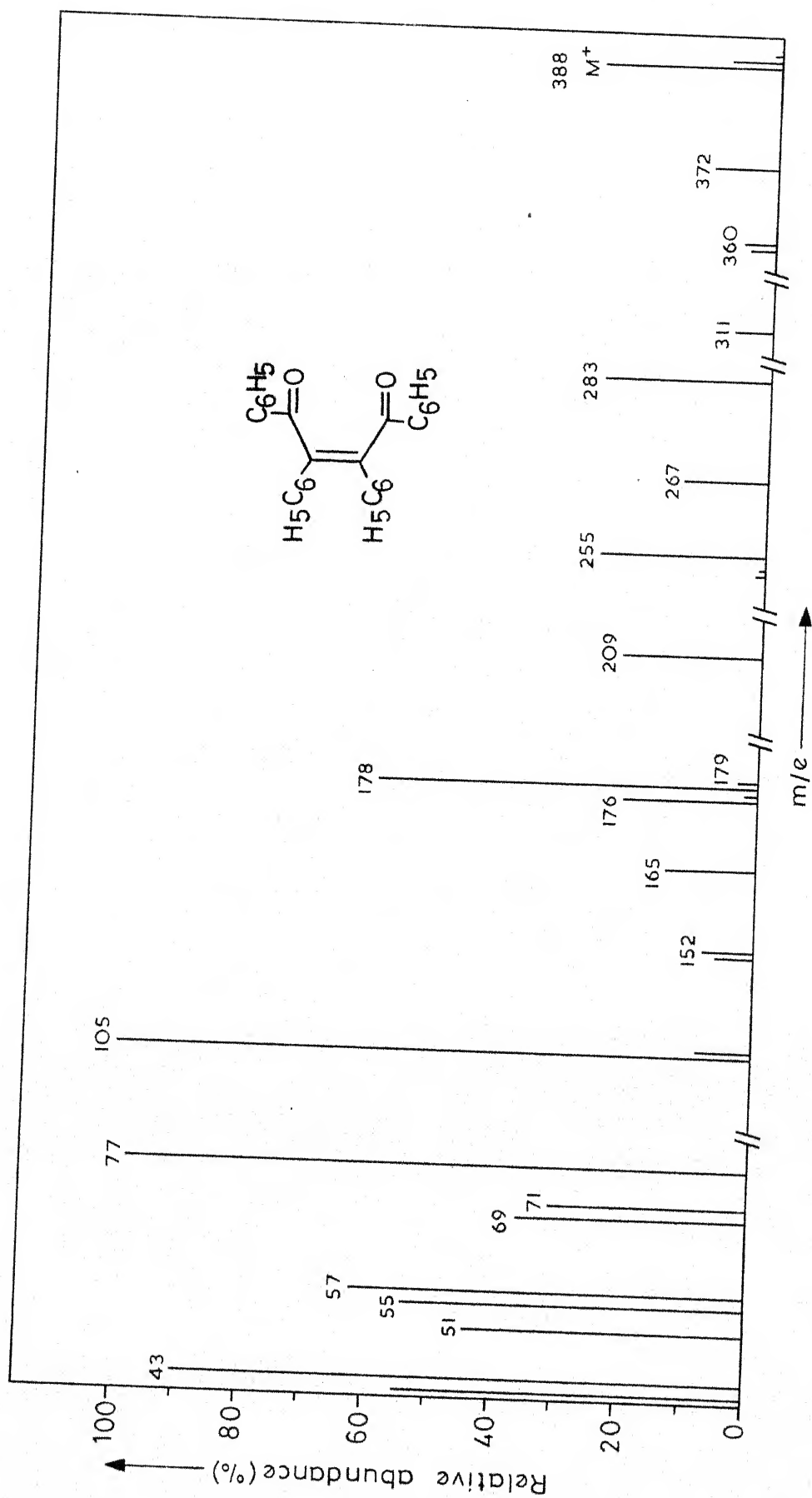
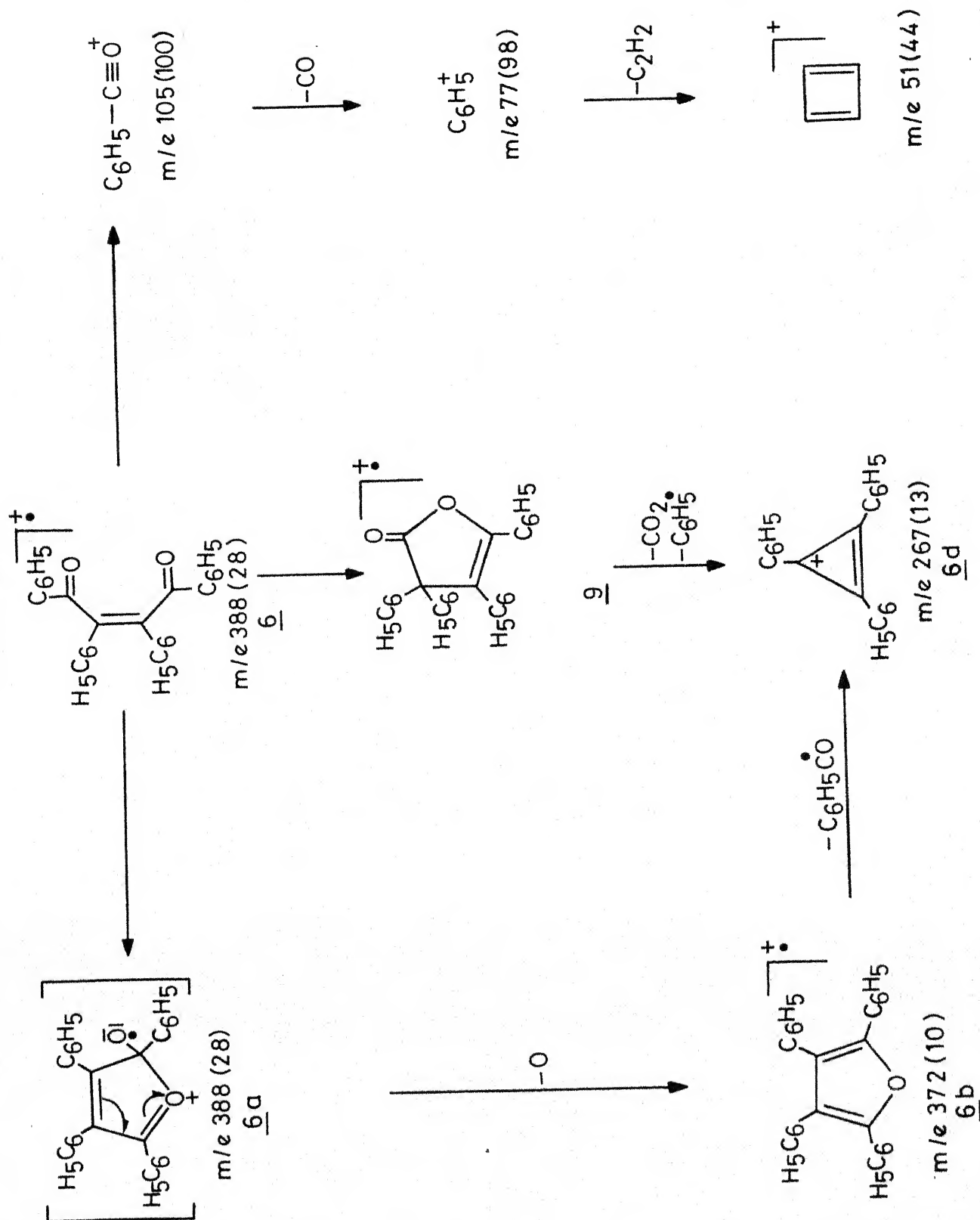


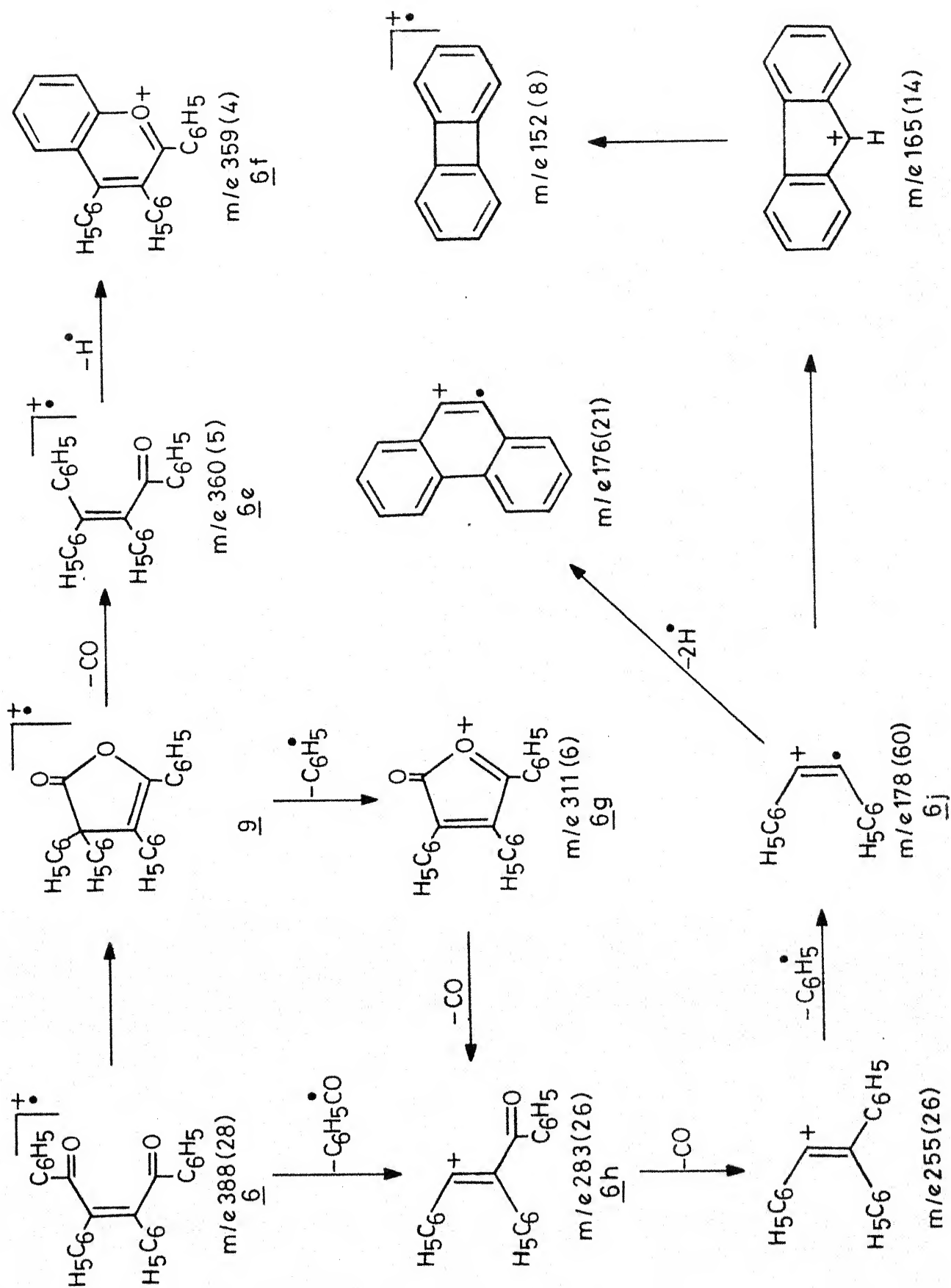
Fig. I. 8 Mass spectrum of cis-1,2-dibenzoylstilbene (6)



Scheme 1.16



Scheme 1.16 (Contd)



of fragmentation that had been observed was the loss of a benzoyl group by  $\alpha$ -cleavage, from the starting compound to give a fragment 6h at  $m/e$  283. The peak at  $m/e$  360 could be assigned to the fragment 6e, formed through the loss of CO from the intermediate lactone 9, which in turn, could be formed through the pericyclic transformation of the starting diketone.

With a view to assessing whether at least some of the fragments observed in the mass spectrum of 6 arose through the lactone intermediate 9, the mass spectrum of 2,2,3,4-tetraphenylbut-3-enolide (9) was examined separately. The mass spectrum of 9 (Fig. I.9) showed the molecular ion peak at  $m/e$  388 (100). Other peaks were observed at  $m/e$  360 (91), 359 (65), 344(11), 311(11), 283(76), 267(17), 265(15), 255(93), 253(45), 252(45), 239(21), 227(6), 209(3), 178(39), 163(20), 151(32), 152(33), 139(18), 130(10), 126(21), 105(90), 77(88), 55(42) and 51(69), which could be assigned to some of the fragments shown in Scheme I.17. It is interesting to note that several peaks in the mass spectrum of 6 correspond to the fragments observed in the mass spectrum of the lactone 9, indicating thereby that 6 undergoes at least partial transformation to 9 under electron impact, similar to the observed thermal mode of transformation of 6.

The mass spectrum of 2,3-dibenzoylbicyclo[2.2.1]-hepta-2,5-diene (14) showed the molecular ion peak at  $m/e$  300 (100) (Fig. I.10). Other peaks in the spectrum were

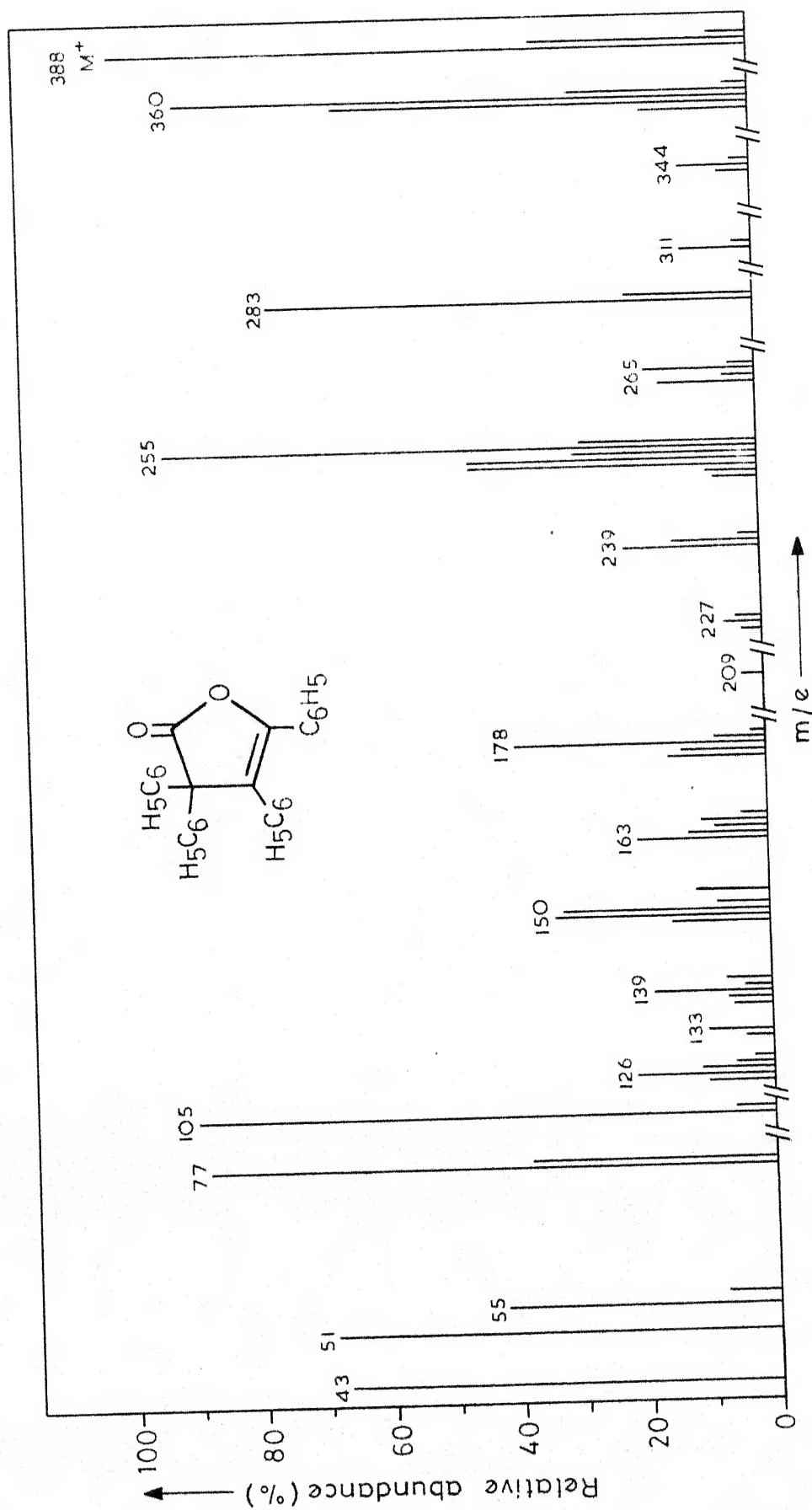
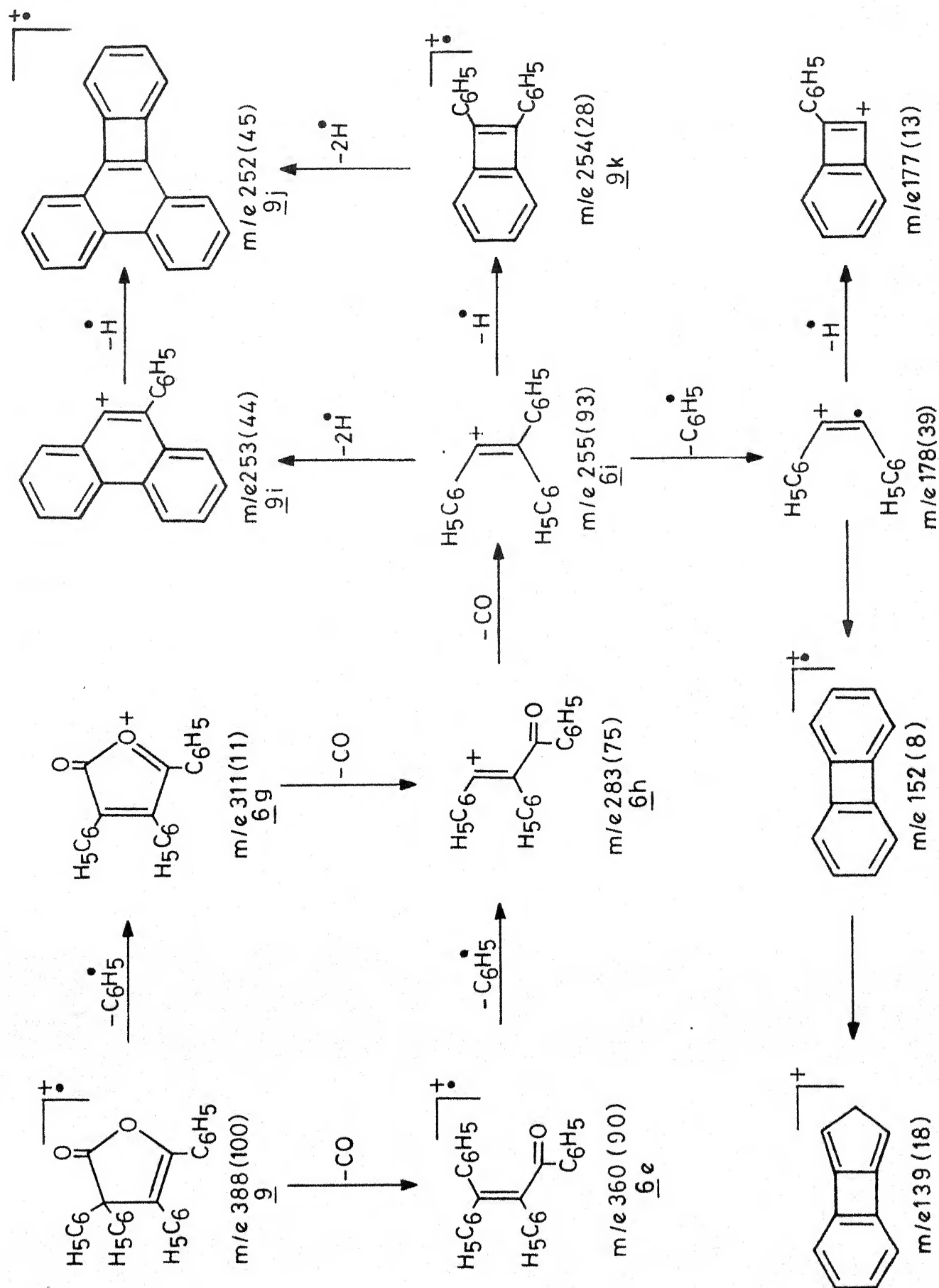


Fig.I.9 Mass spectrum of 2,2,3,4-tetraphenyl-but-3-enolide (9)



Scheme 1.17 (Contd)



observed at  $m/e$  272 (5), 235 (12), 223 (4), 178 (3), 165 (10), 152 (5), 105 (38), 77 (34) and 66 (18), which could be assigned to some of the fragments shown in Scheme I.18. One of the fragmentation modes of 14 involved the loss of CO to give a fragment 14b at  $m/e$  272. The formation of this fragment could be rationalized in terms of the intermediate 14a, arising through a pericyclic ring closure of the starting diketone 14. The fragment 14b itself undergoes further fragmentation to give different species as indicated in Scheme I.18. A second mode of fragmentation of 14 is through  $\alpha$ -cleavage, involving the loss of a phenyl group and perhaps leading to the intermediate 14g at  $m/e$  223, which in turn can lose CO to give the fragment 14h at  $m/e$  195. A major mode of fragmentation of 14 is through a retro-Diels-Alder type reaction leading to the fragment 14n at  $m/e$  66. A significant fragment 14h, at  $m/e$  235 was formed through a retro-Diels-Alder reaction of 14 with hydrogen transfer. Similar examples of retro-Diels-Alder reactions with hydrogen transfer have been reported in the literature.<sup>37-39</sup> The peak at  $m/e$  105 can be assigned to a benzoyl fragment which is indicative of the loss of benzoyl group either from 14 or some of its fragments.

The mass spectrum of 2,3-dibenzoylbicyclo[2.2.2]-octa-2,5-diene (15) showed a molecular ion peak at  $m/e$  314 (67) (Fig. I.11). Other significant peaks were observed at  $m/e$

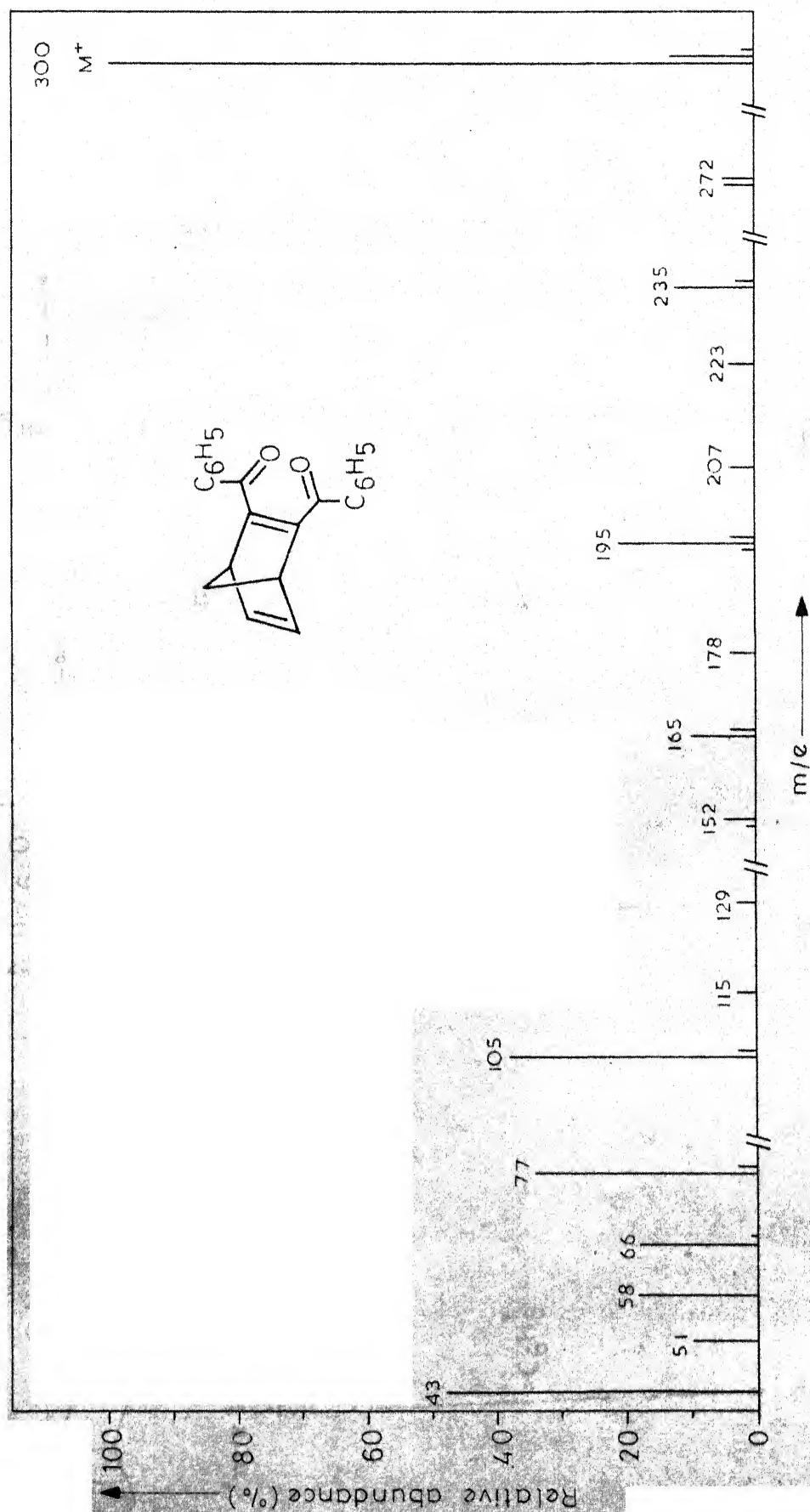
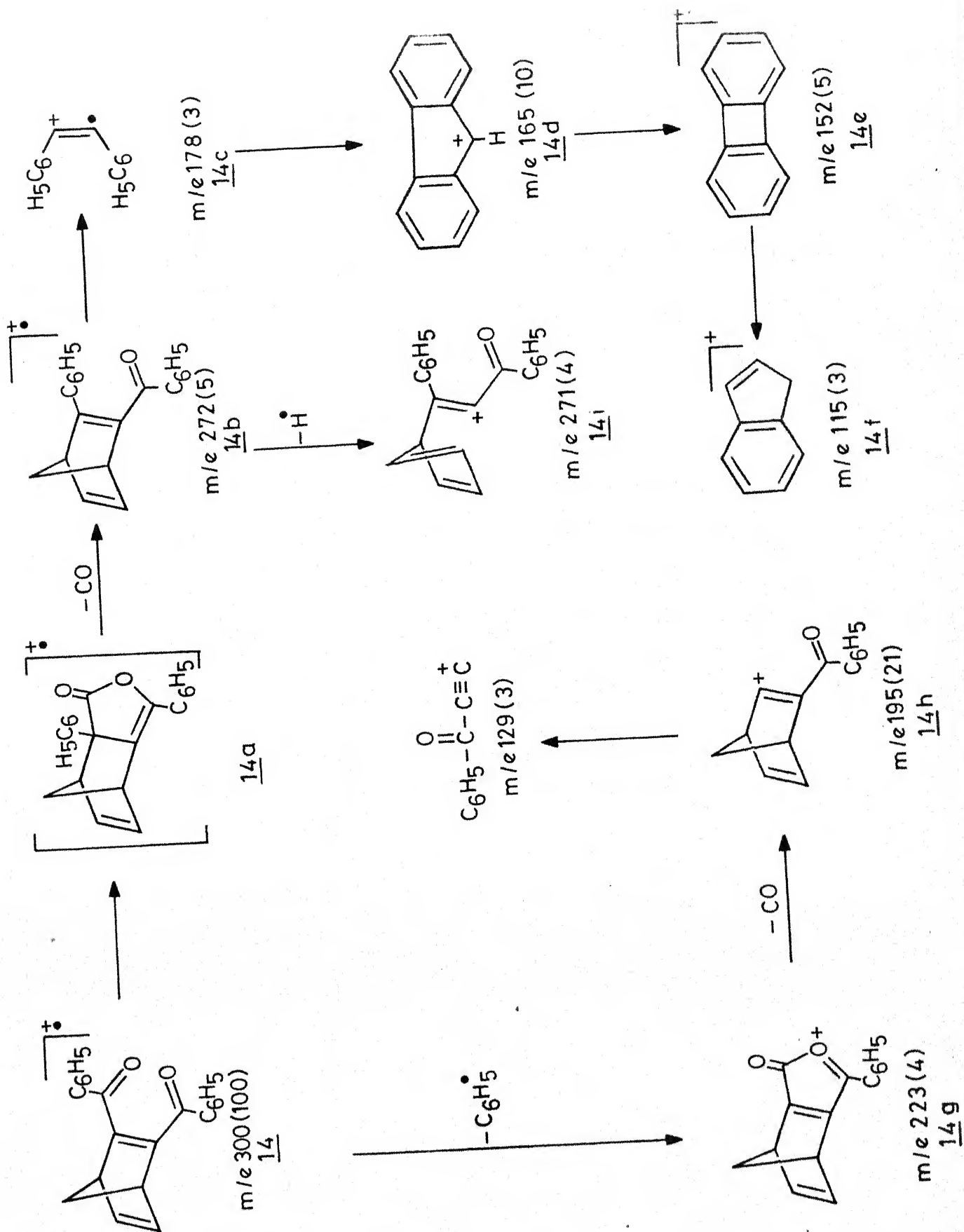


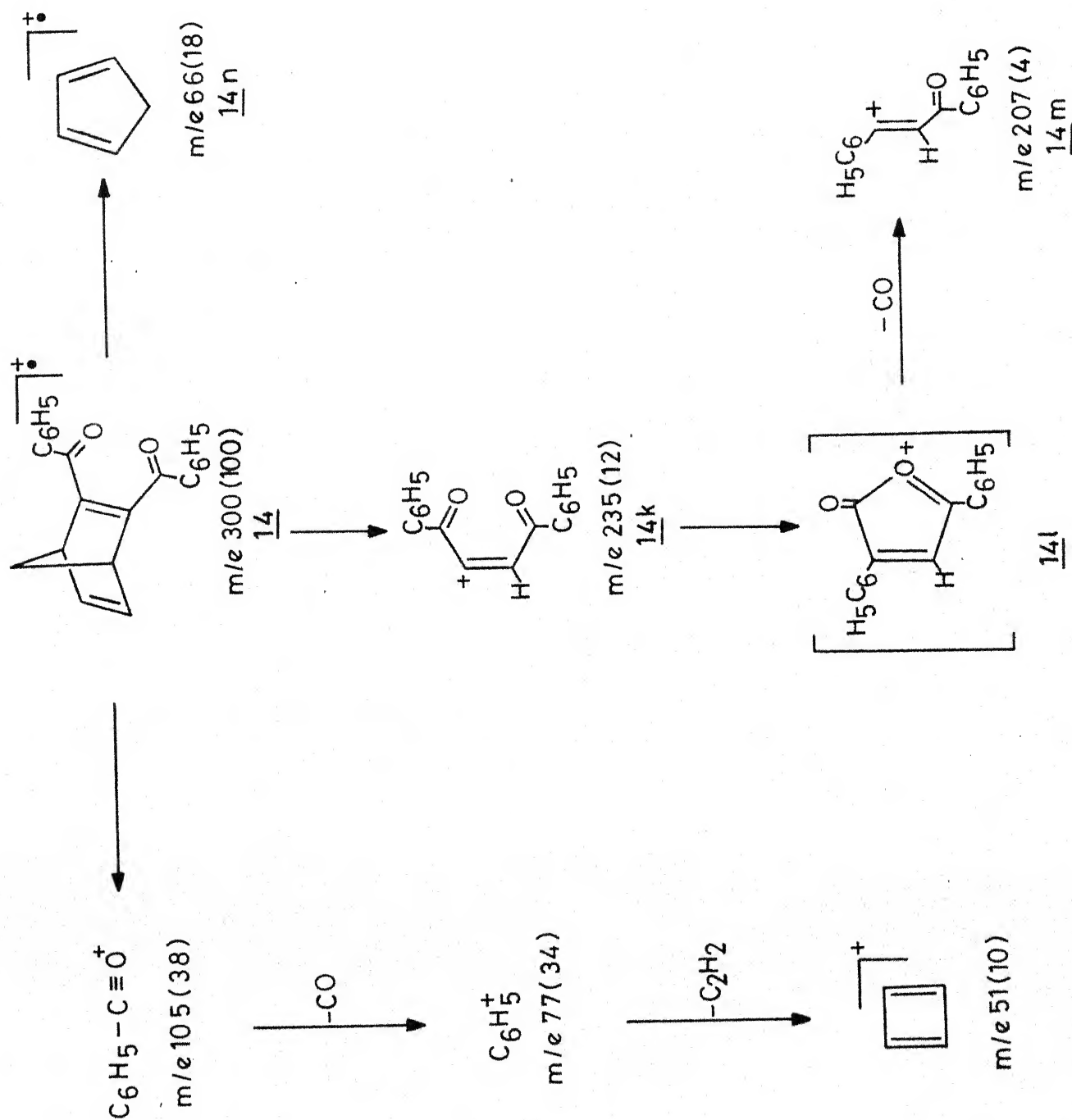
Fig.I. 10 Mass spectrum of 2,3-dibenzoylbicyclo [2.2.1]hepta-2,5-diene (14)



Scheme 1.18



Scheme 1.18 (Contd.)



286(60), 248(5), 209(100), 189(7), 152(10), 105(50) and 77(25), which could be assigned to some of the fragments shown in Scheme I.19. The prominent peak at  $m/e$  286 was attributed to 1,2-dibenzoylbenzene (39), arising through a retro-Diels-Alder elimination of ethylene from 15. It may be pointed out in this connection that a similar loss of ethylene fragment was also observed during the thermal transformation of 15. The most prominent peak in the spectrum of 15 was observed at  $m/e$  209(100), which might arise through the loss of a phenyl radical from 39 to give 15e. The fragment at  $m/e$  258 could be rationalized in terms of 15e, formed by the loss of CO from the lactone intermediate 15b, which in turn is formed from 39.

We have examined the mass spectrum of 1,2-dibenzoylbenzene (39) also to ascertain whether the fragmentation modes of 15 correspond to some of the fragments due to 39. It was interesting to note that the mass spectrum of 39 (Fig. I.12) showed several peaks at  $m/e$  286(32), 258(3), 209(100), 193(3), 181(6), 165(4), 152(30), 105(37), 77(37) and 51(15), corresponding to some of the peaks observed in the spectrum of 15. Scheme I.20 indicates some of the major fragmentation modes of 39.

The mass spectrum of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]-hepta-2,5-diene (16) (Fig. I.13) showed a low intensity molecular ion peak at  $m/e$  302(15). Other peaks were

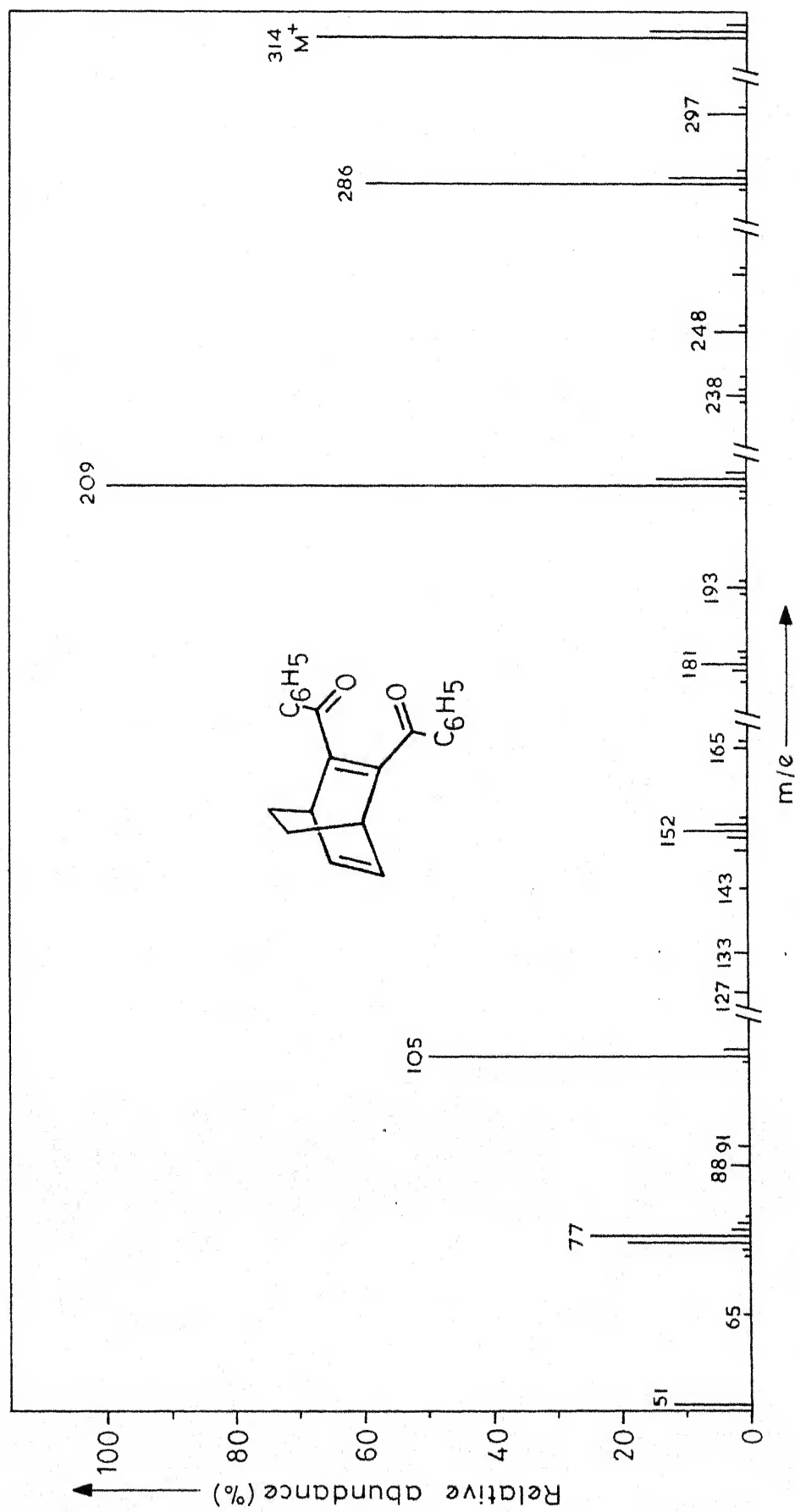
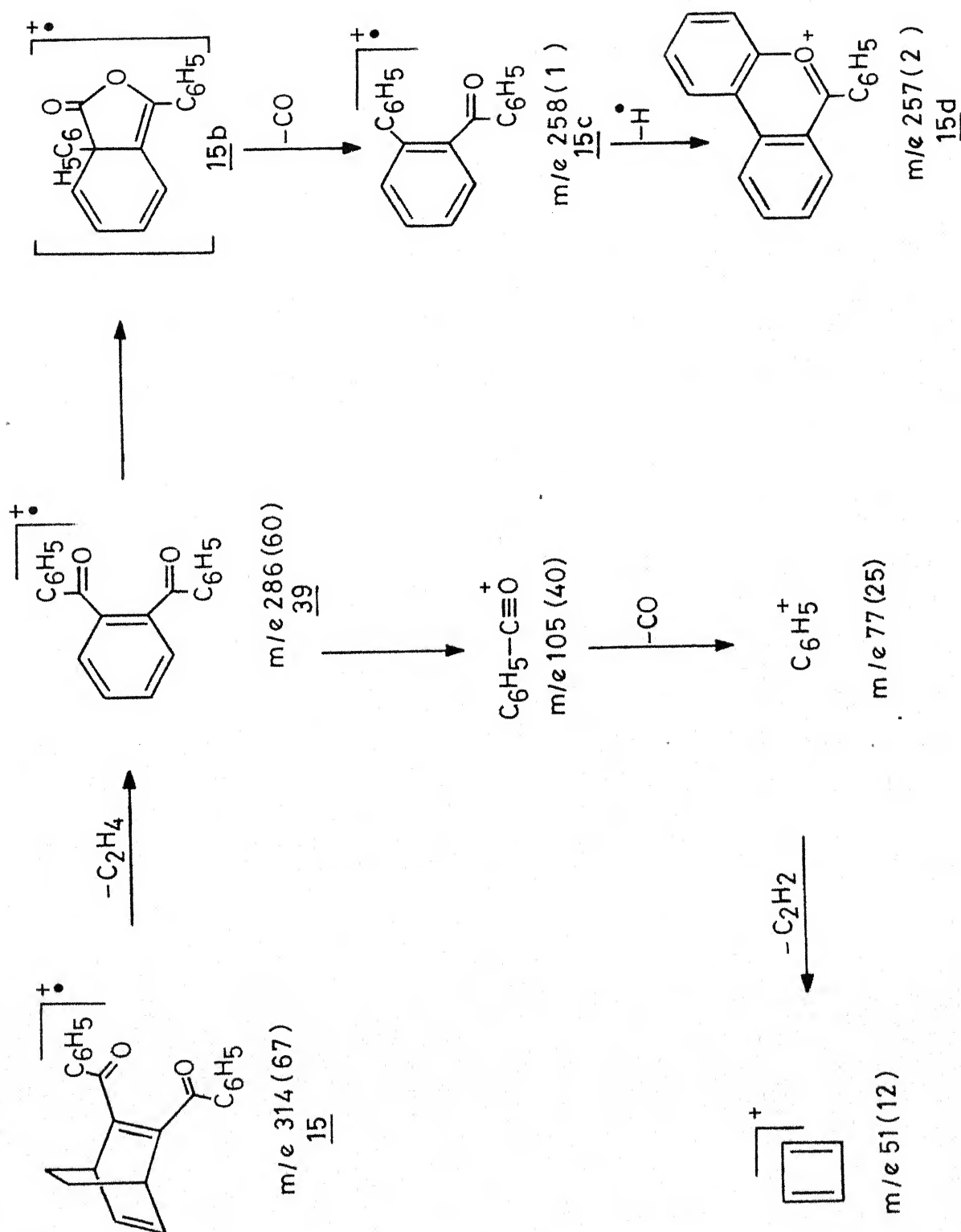


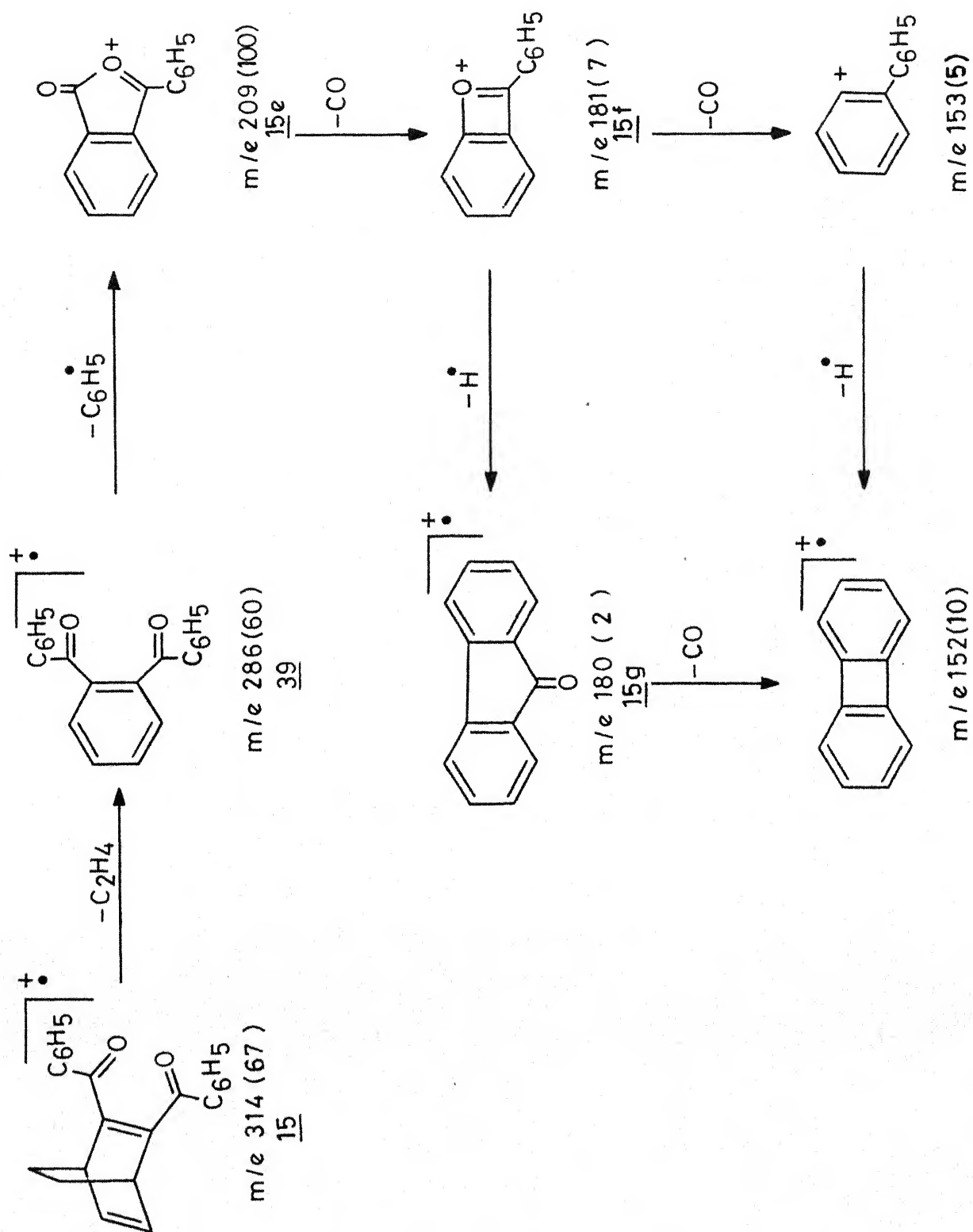
Fig.I. 11 Mass spectrum of 2,3-dibenzoylbicyclo [2.2.2]octa-2,5-diene (15)

Scheme 1.19



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Scheme 1.19 (Contd)



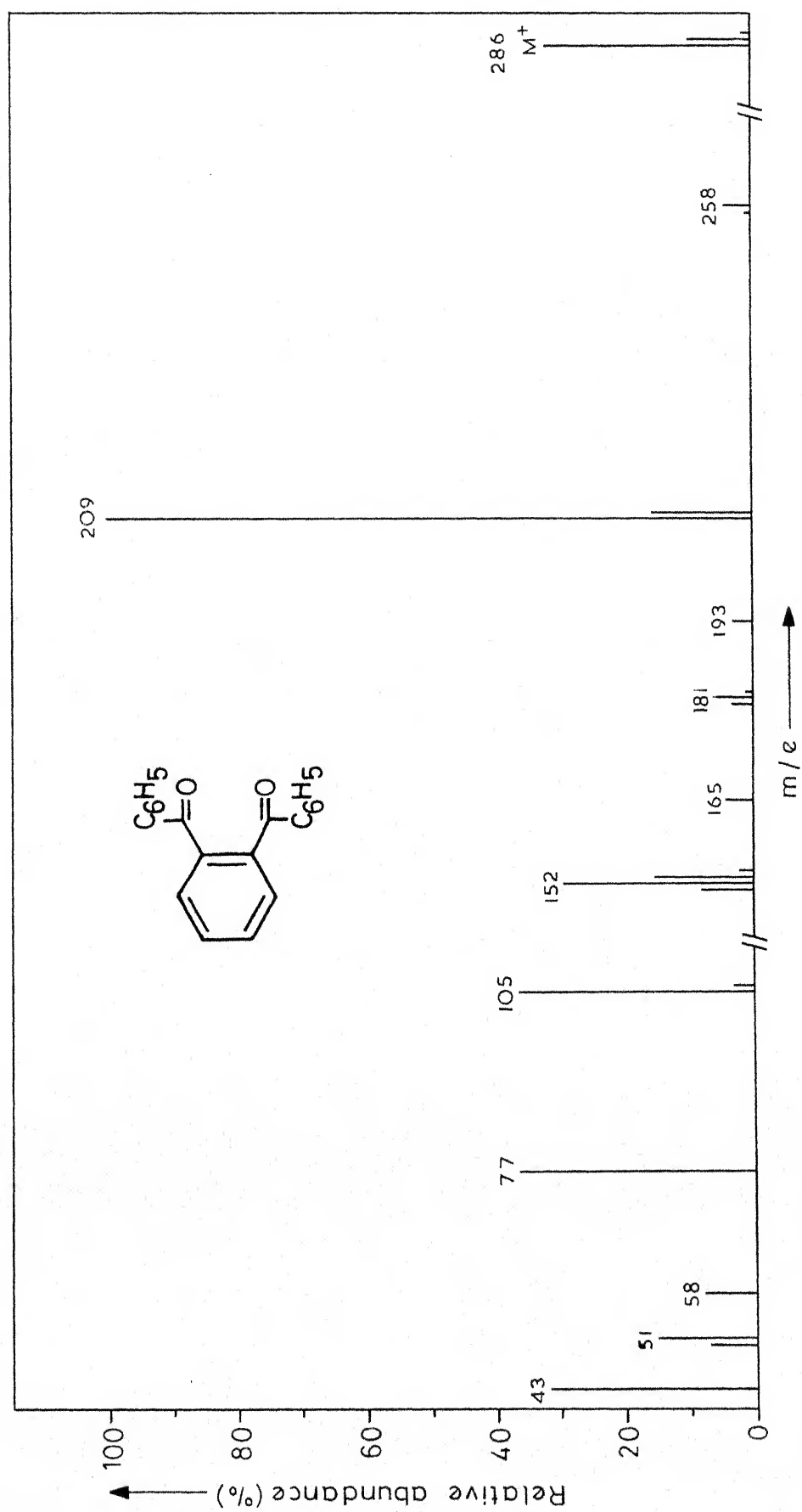
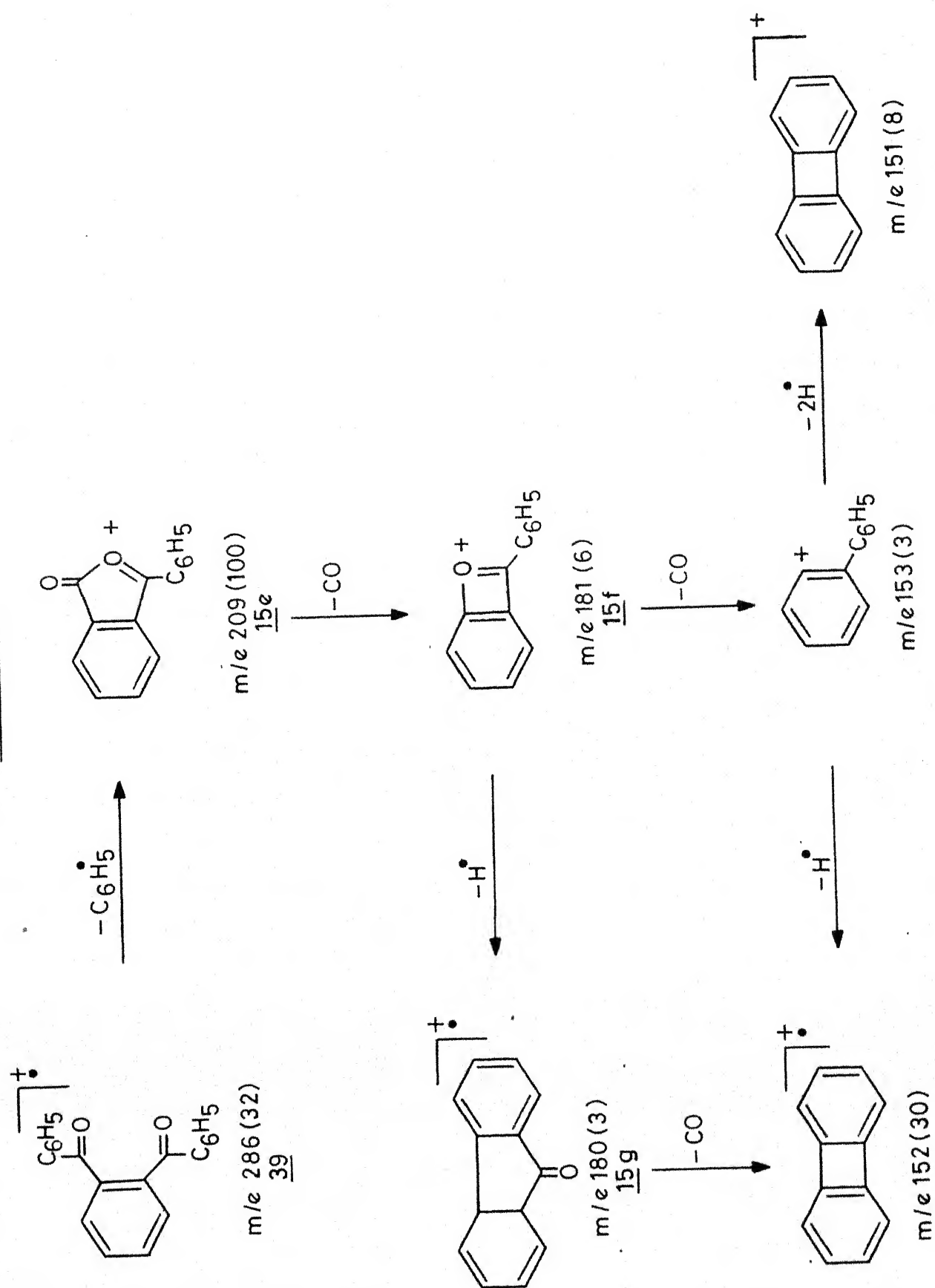


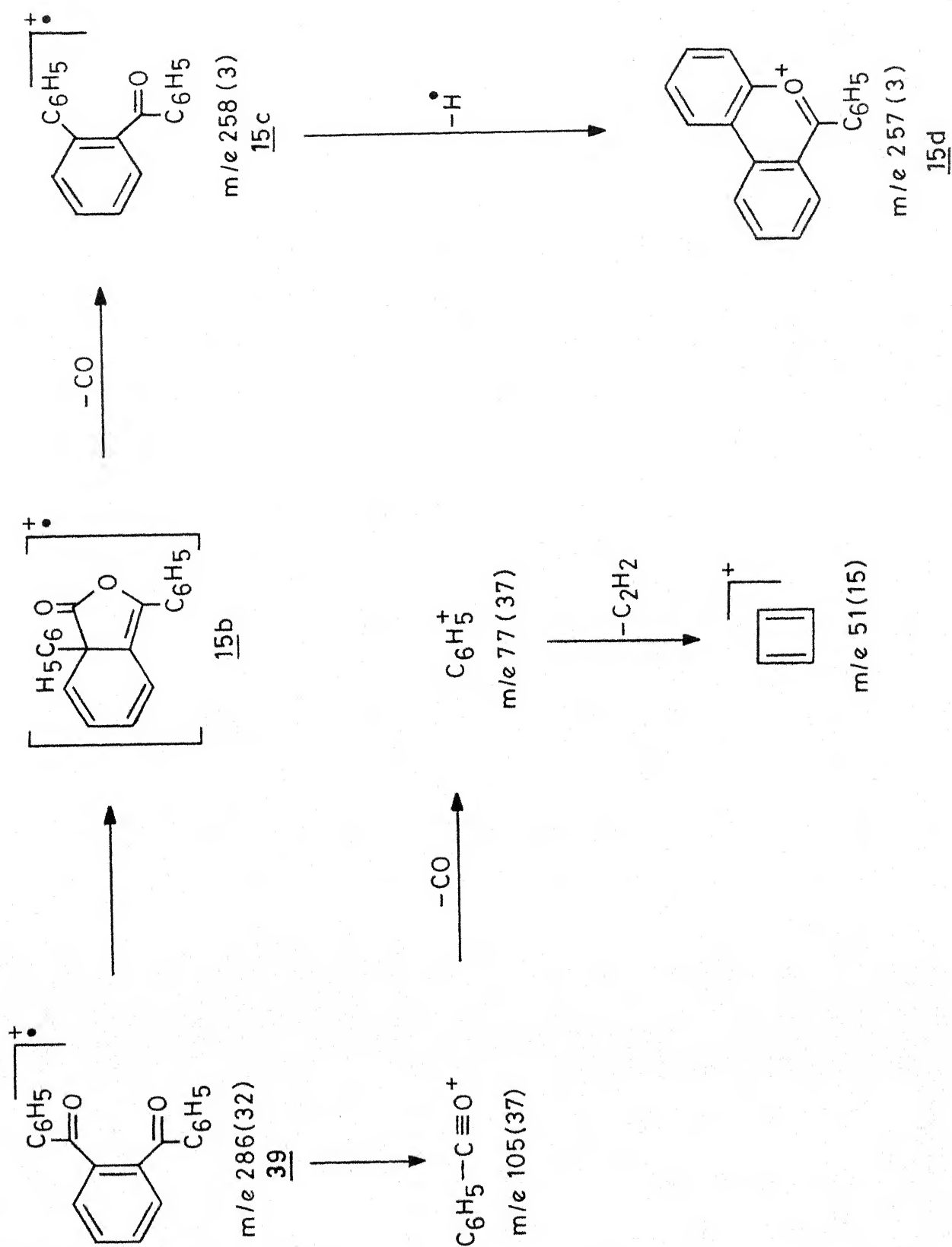
Fig.I.12 Mass spectrum of 1,2-dibenzoylbenzene (39)

Scheme 1.20





Scheme 1.20(Contd)



observed at  $m/e$  286(2), 273(16), 234(87), 209(2), 206(11), 205(11), 197(13), 178(34), 152(4), 151(4), 129(34), 105(100), 77(65) and 68(81). Some of these fragmentation modes have been rationalized in Scheme I.21. One of the pathways appears to involve the loss of CO from 16 to give the fragment 16b at  $m/e$  274, and 16a may be an intermediate in this transformation. A second mode of fragmentation is through the loss of a benzoyl group from 16 to give the fragment 16d at  $m/e$  197, which could also result from the loss of a phenyl radical from 16b. Further loss of a benzoyl group from 16b would lead to the intermediate 16c at  $m/e$  169. The loss of acetylene and a phenyl radical from 16 would give rise to the fragment 16g at  $m/e$  199. An interesting mode of fragmentation of 16 involves the loss of an oxygen atom, and perhaps leading to the fragment 16h at  $m/e$  286. Similar loss of oxygen atoms have been observed in the mass spectral fragmentations of 1,4-dihydro-1,4-epoxynaphthalene<sup>40</sup> and dibenzo-1,4-dioxin.<sup>41</sup> In the case of 16, the driving force for oxygen elimination may be the gain in stabilization due to the formation of 1,2-dibenzoylbenzene (39). The peak at  $m/e$  209 has been attributed to the fragment 16i formed from 39 through a known fragmentation mode. Yet another mode of fragmentation of 16 is through a retro-diels-Alder type, as evidenced by the formation of fragments 16j at  $m/e$  235 and 16p at  $m/e$  68. Further fragmentation of these intermediates would

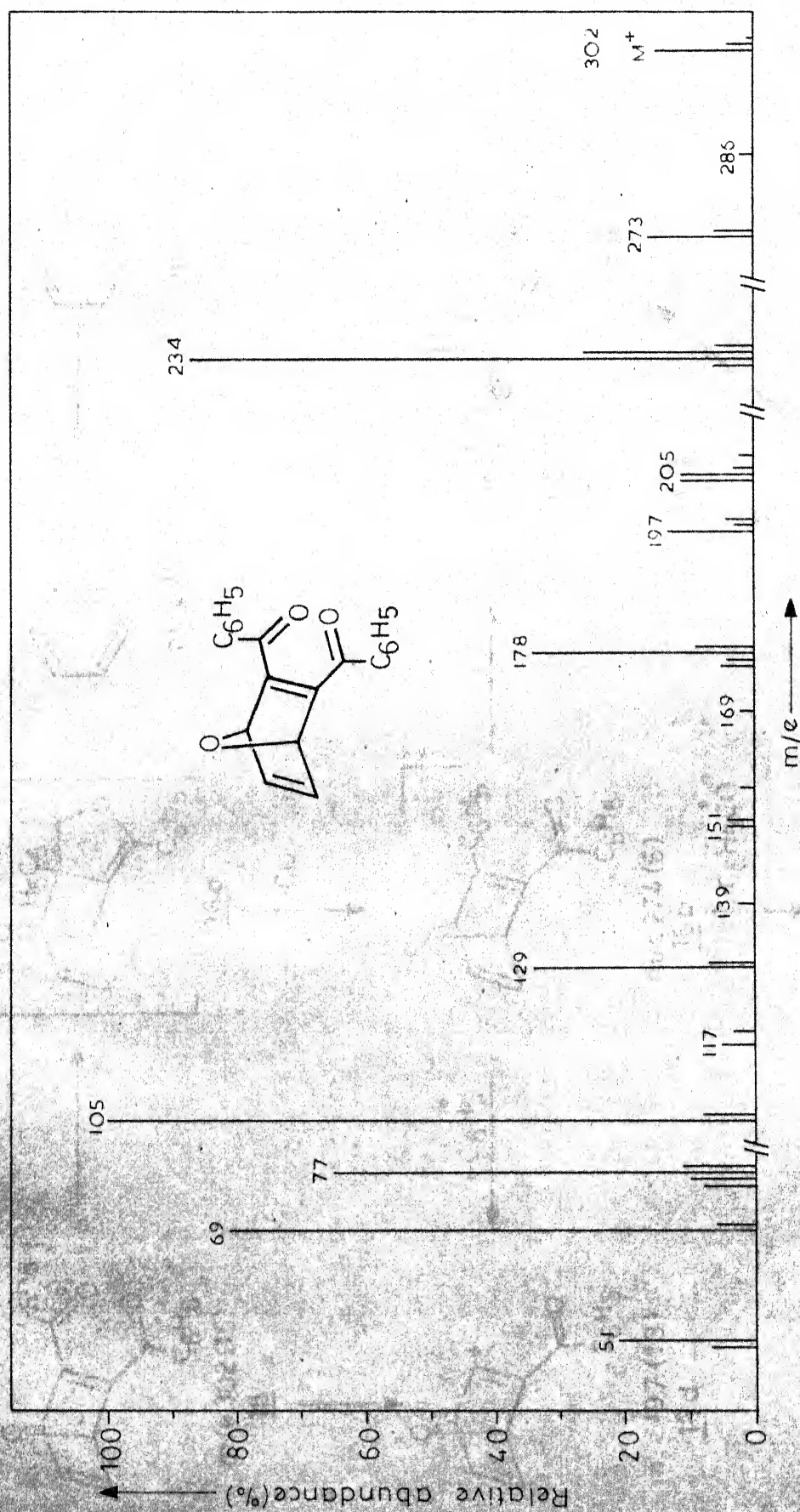
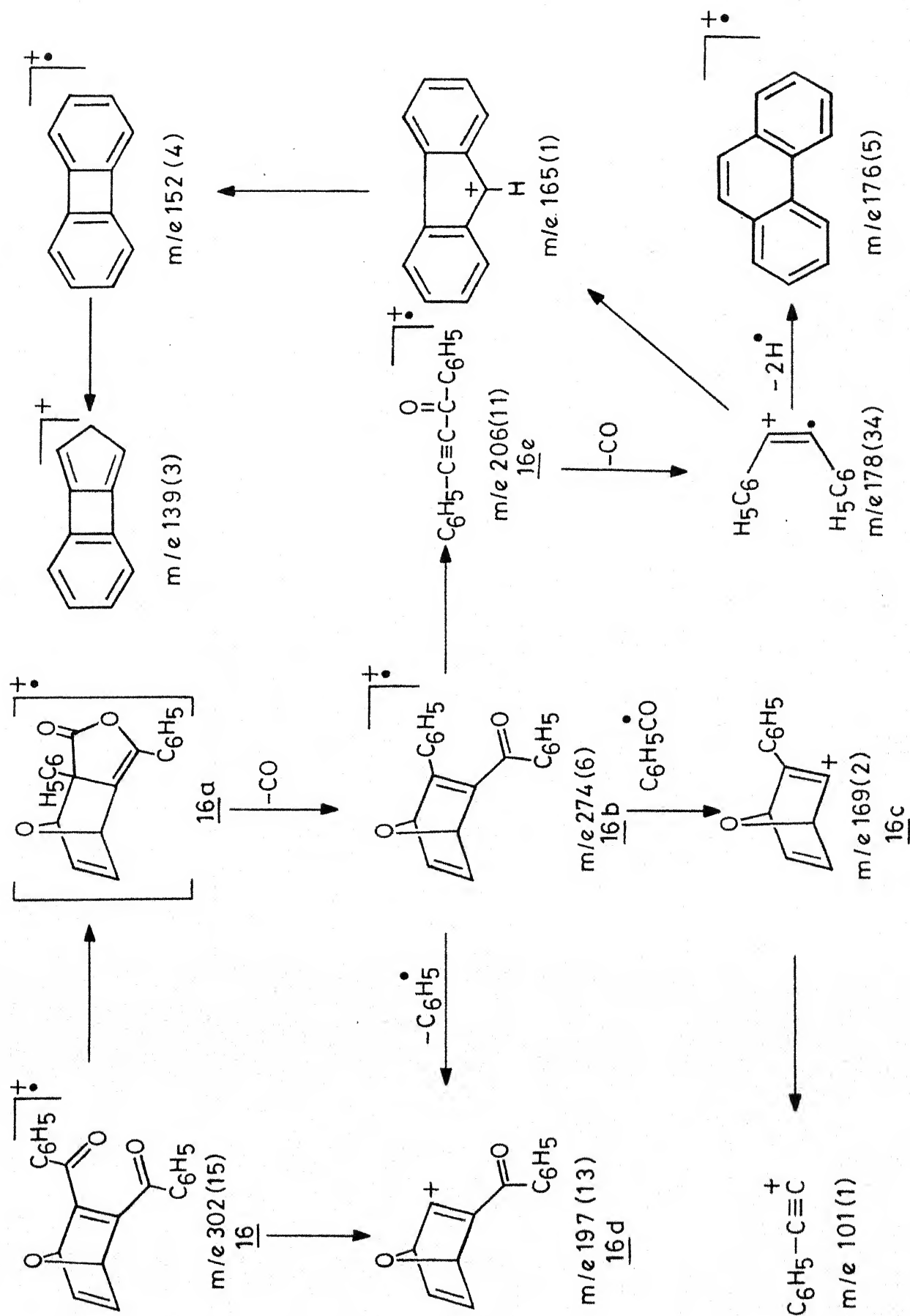


Fig. I. 13 Mass spectrum of 7-oxa-2,3-dibenzoylbicyclo [2.2.1]hepta-2,5-diene(16)

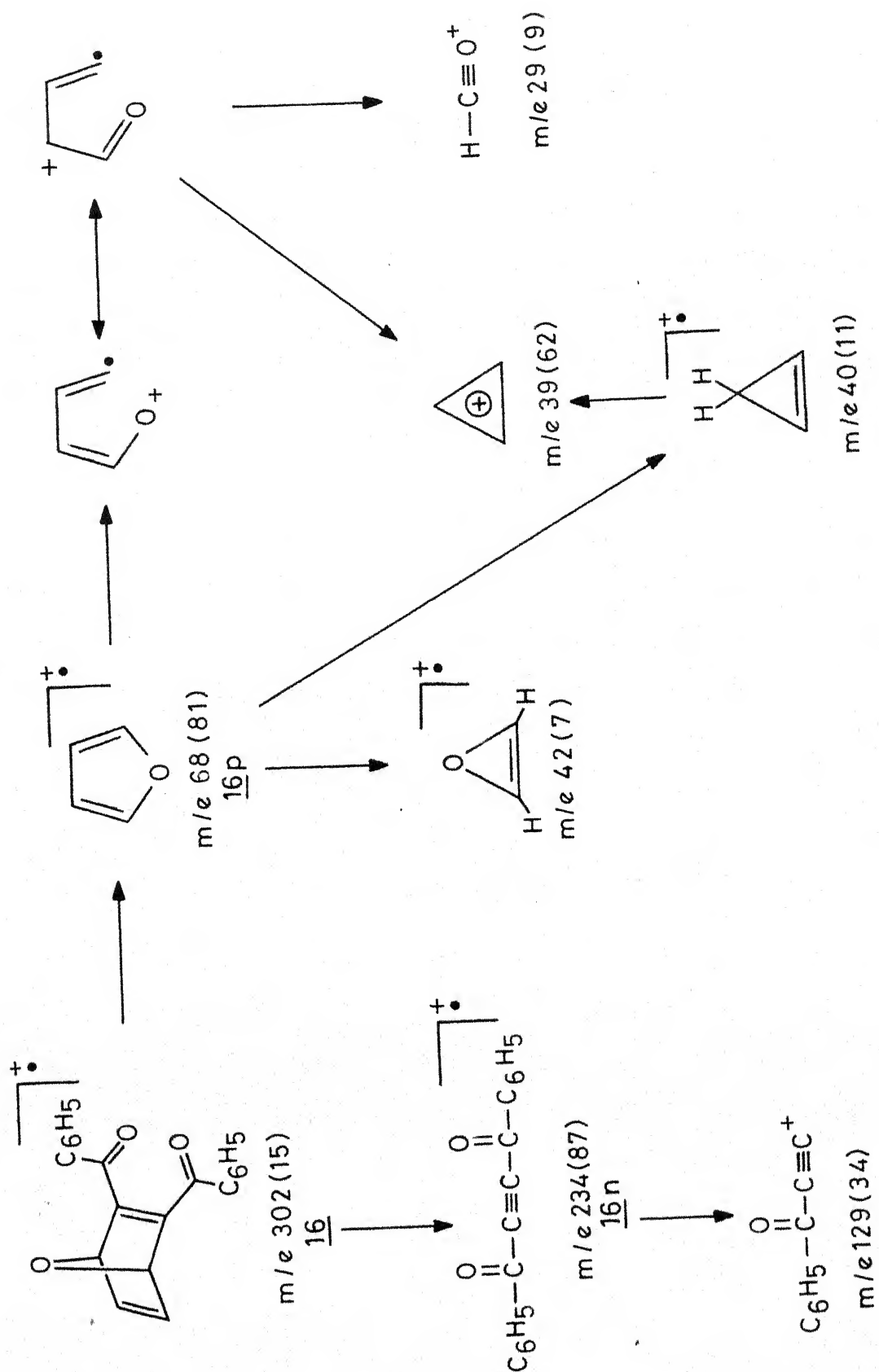
Scheme 1.21



Scheme 1.21(Contd)



Scheme 1.21 (Contd)



lead to other peaks observed in the mass spectrum of 16, as shown in Scheme I.21.

As in the case of 16, the mass spectrum of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18) (Fig. I.14) showed a low intensity molecular ion peak at  $m/e$  504(5). Other peaks in the spectrum were observed at  $m/e$  399(9), 382(4), 297(3), 270(100), 239(5), 234(15), 209(4), 193(3), 178(5), 165(5), 135(15), 129(5), 105(35), 77(15) and 51(4) and these are assigned to some of the fragments shown in Scheme I.22. A major mode of fragmentation of 18 has been through the retro-Diels-Alder reaction, leading to the 1,3-diphenylisobenzofuran fragment, 18a observed at  $m/e$  270(100). The peaks at  $m/e$  269, 241, 239, 193 and 165, could be assigned to fragments like 18c, 18d, 18e, 18f and 18g, formed from further fragmentation of 18a. In this connection it might be mentioned that recent studies have shown that similar fragments are observed in the mass spectrum of 1,3-diphenylisobenzofuran.<sup>16</sup> As in the case of 16, one of the fragmentation modes of 18, involves the loss of an oxygen atom, to give the fragment 18h at  $m/e$  488. Subsequent loss of a benzoyl group from 18h would lead to the fragment 18i at  $m/e$  383 and then the loss of one hydrogen atom would give rise to the fragment 18j at  $m/e$  382. Loss of a benzoyl group from 18, on the other hand, would lead to the fragment 18n, observed at  $m/e$  399. In



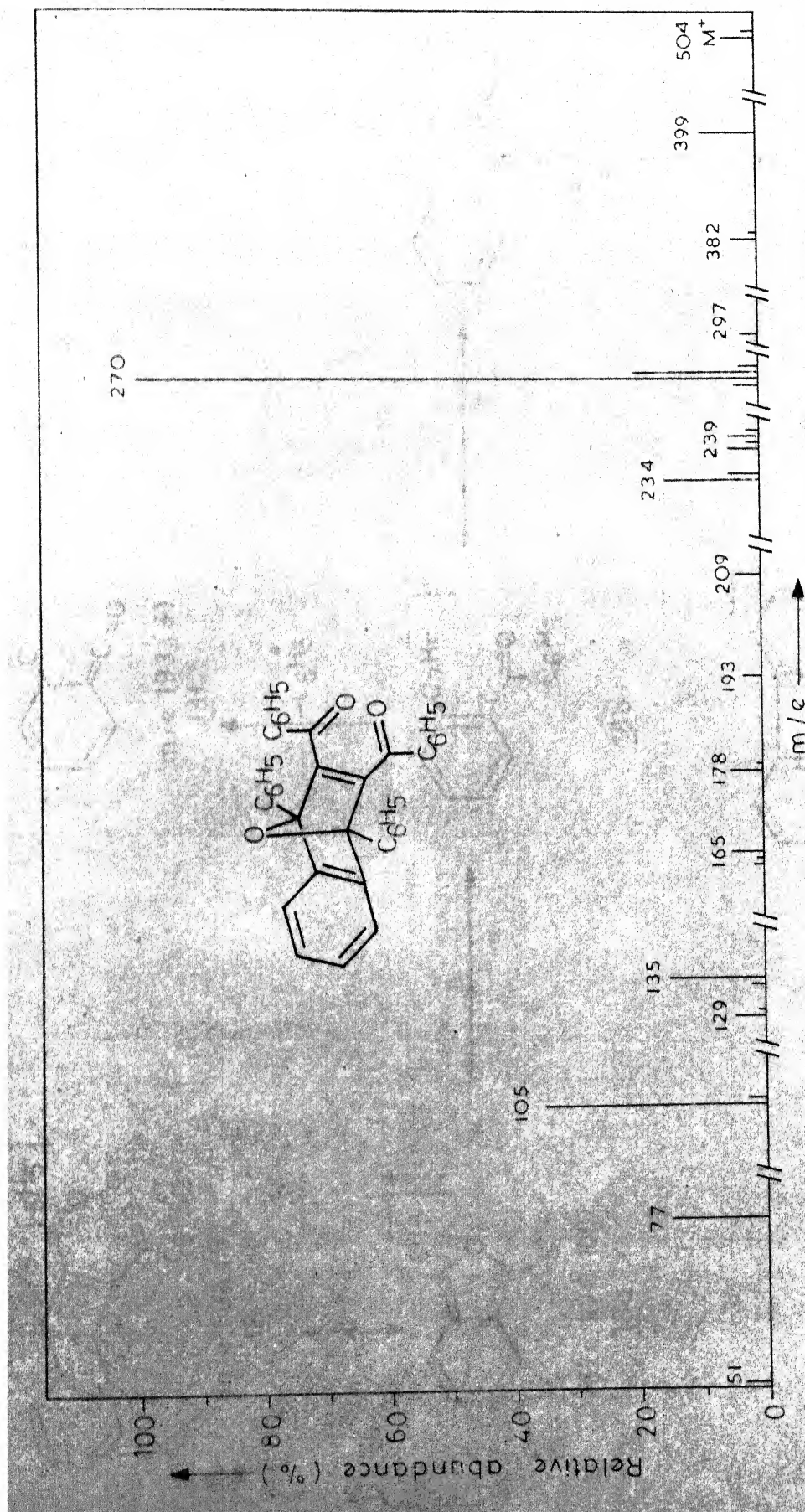
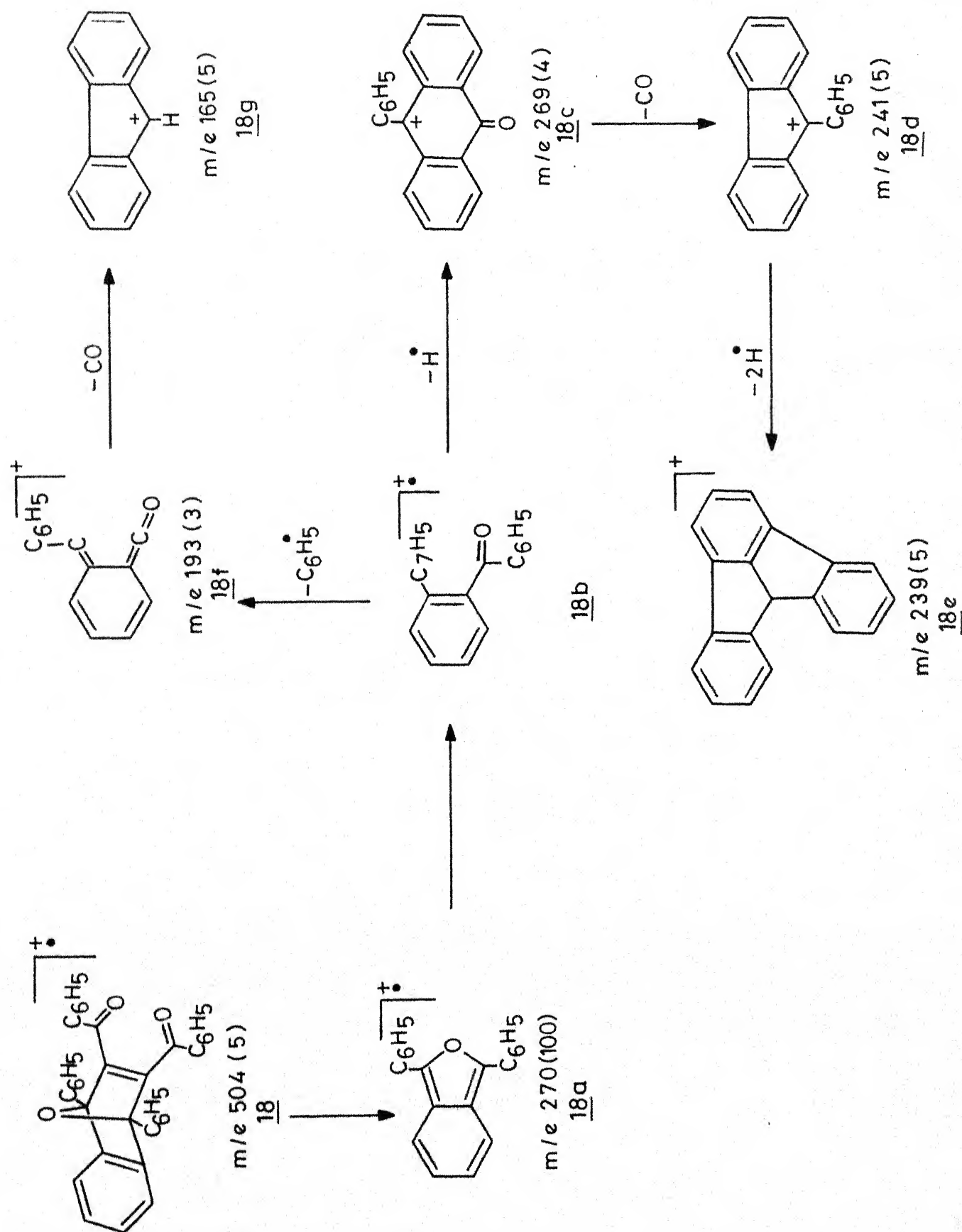
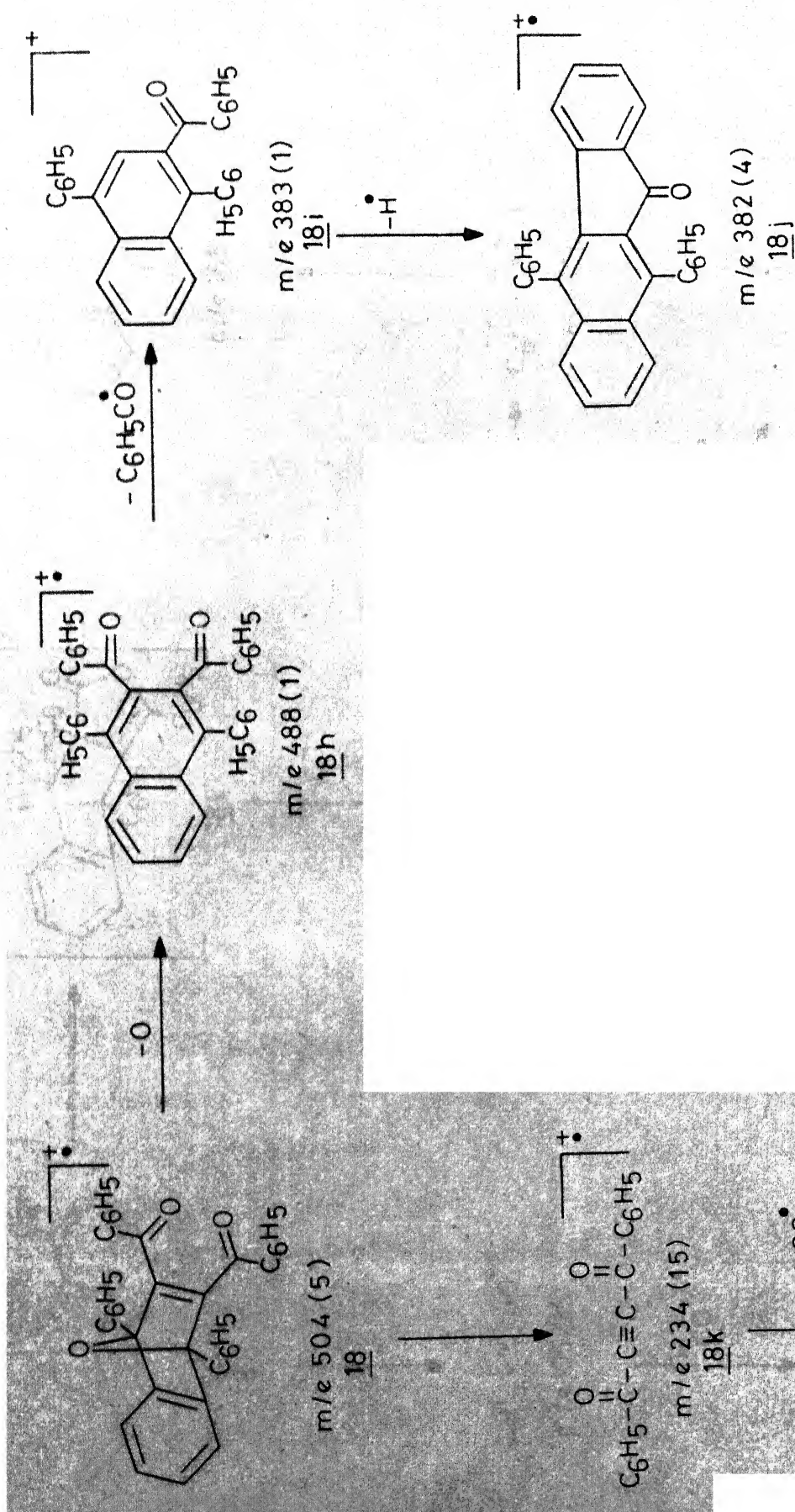


Fig.I.14 Mass spectrum of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene(18)

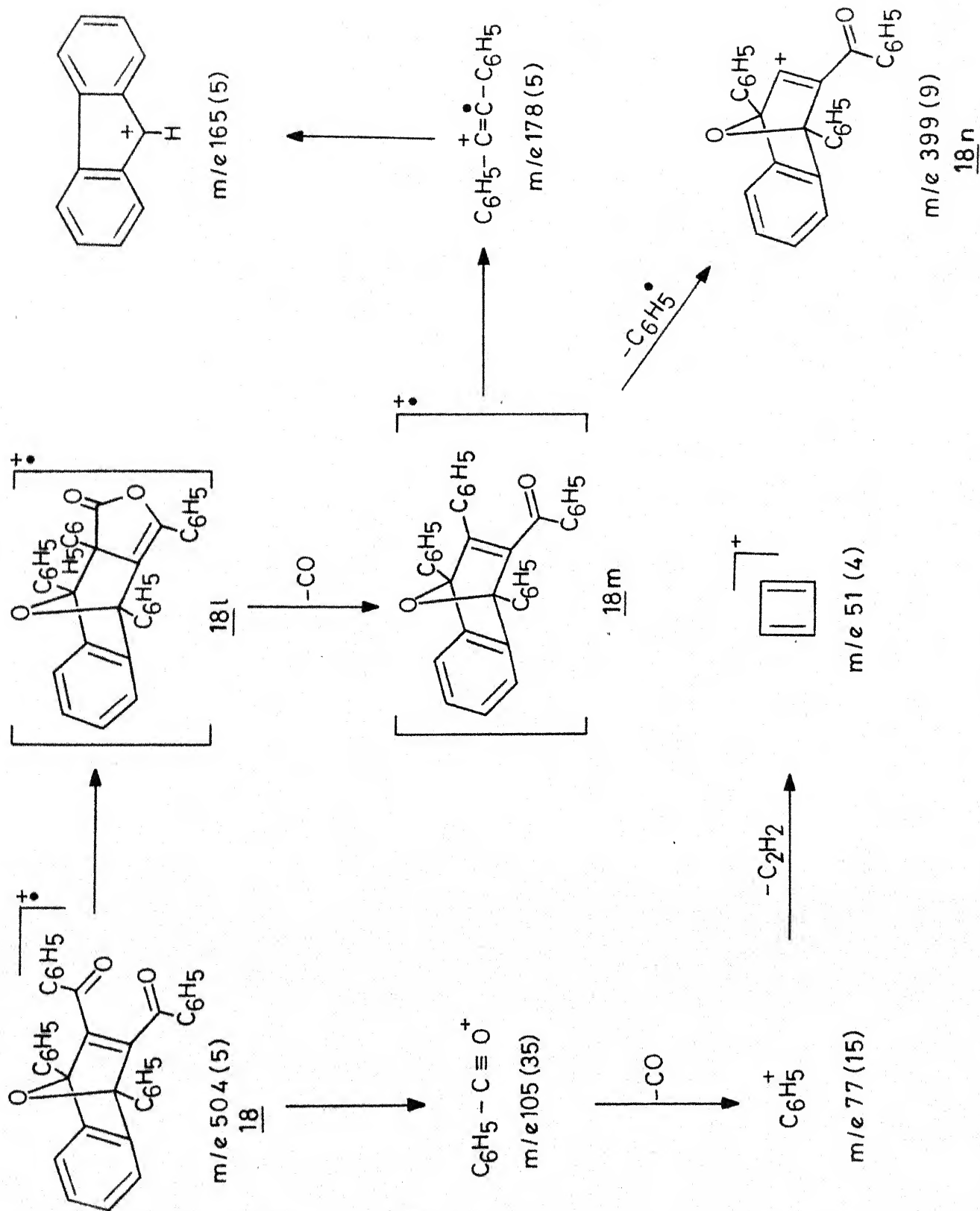
Scheme 1.22



Scheme 1.22 (Contd)



Scheme 1.22 (Contd)



the light of the information concerning the fragmentation mode of 16, it is reasonable to assume that 18n might be formed through intermediates like 18l and 18m as shown in Scheme I.22.

The mass spectrum of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20) (Fig. I.15) showed a prominent molecular ion peak at  $m/e$  412 (83). Other peaks were observed at  $m/e$  332 (9), 308 (8), 307(27), 279(18), 243(6), 202(14), 200(12), 178(65), 166(7), 164(6), 105(100), 77(20) and 51(5). One of these fragmentation modes involves the loss of a benzoyl group from 20 to give the fragment 20b at  $m/e$  307(27), which in turn could lead to fragments like 20c at  $m/e$  279 and 20d at  $m/e$  202 (Scheme I.23). The highest intensity peak at  $m/e$  105 (100) had been due to the benzoyl fragment, 20e. The peak at  $m/e$  178(65) could be assigned to an anthracene fragment 20f, arising through a retro-Diels-Alder reaction.

The mass spectrum of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]-nona-6,8-diene (22) (Fig. I.16) revealed several interesting features. The molecular ion peak was observed at  $m/e$  326 (18), whereas other prominent peaks were observed at 325(2), 311(1), 270(7), 249(2), 235(1), 221(33), 204(2), 193(2), 178(2), 165(2), 152(1), 115(4), 105(100), 91(6), 77(30) and 51(20), which could be assigned to some of the fragments shown in Scheme I.24. The peak at  $m/e$  325 has been assigned to the



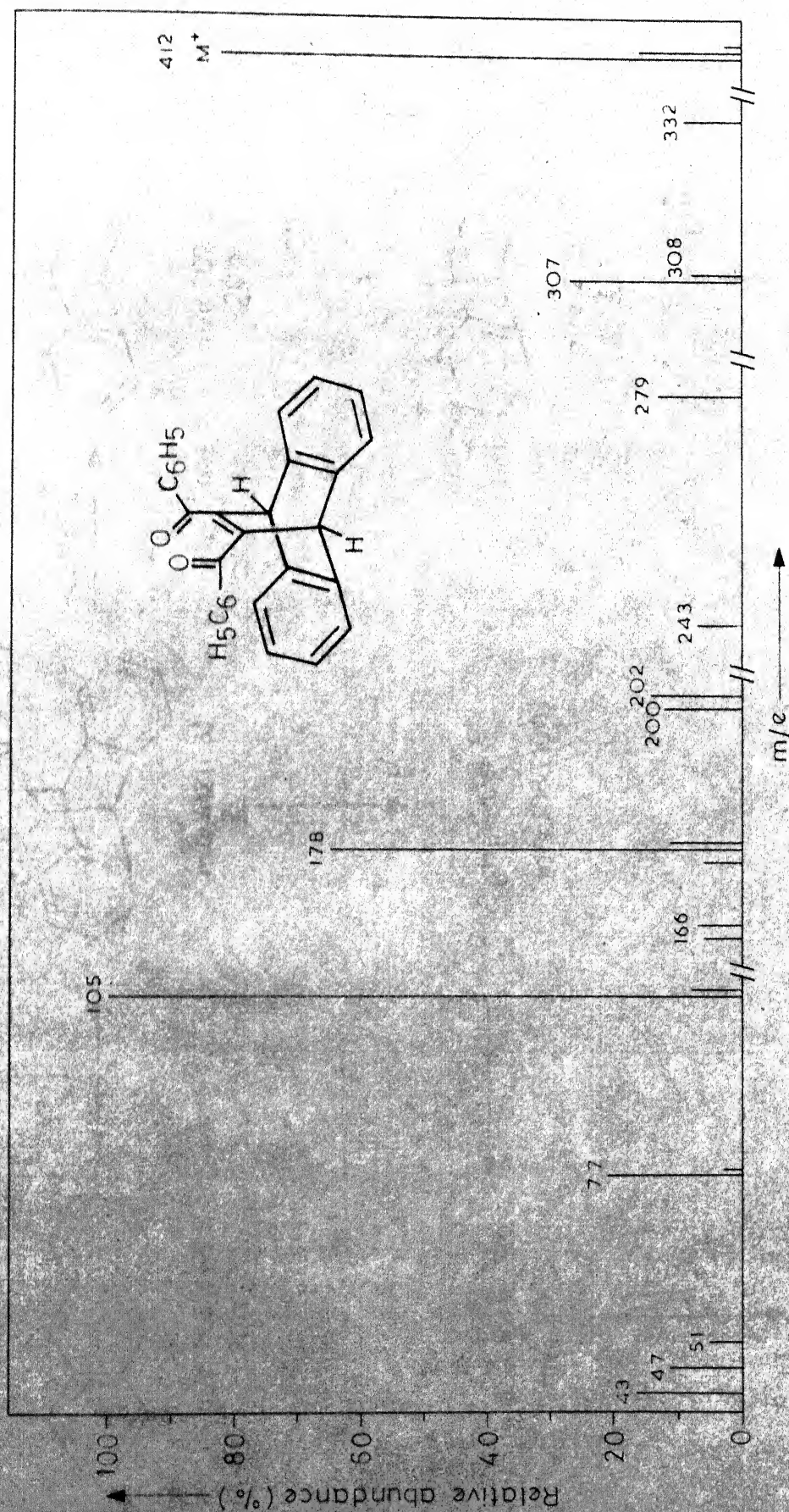
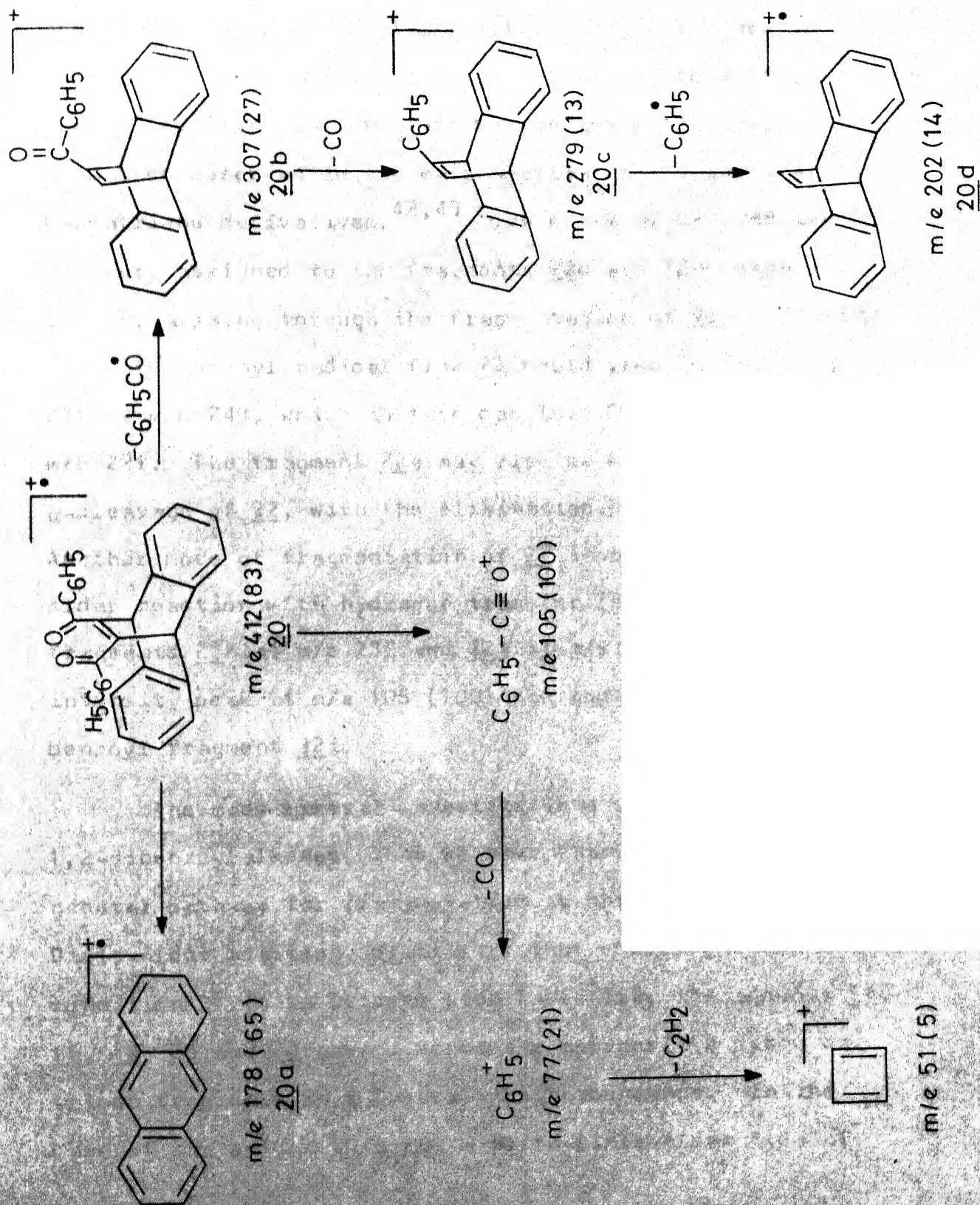


Fig. I. 15 Mass spectrum of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene(20)

Scheme 1.23



fragment 22a, formed by the elimination of one hydrogen atom, whereas the peak at  $m/e$  311 could be assigned to the fragment 22h formed through the loss of one methyl group. Similar loss of hydrogen atom and methyl groups have been observed in the mass spectra of several cycloheptatriene derivatives.<sup>42,43</sup> The peaks at  $m/e$  248 and 220 were assigned to the fragments 22c and 22d respectively, arising through the fragmentation of 22a. Elimination of a phenyl radical from 22 could lead to the fragment 22f at  $m/e$  249, which in turn can lose CO to give 22g at  $m/e$  221. The fragment 22g may also be formed through an  $\alpha$ -cleavage of 22, with the elimination of a benzoyl group. Another mode of fragmentation of 22 involves a retro-Diels-Alder reaction with hydrogen transfer leading to the fragments 22h at  $m/e$  235 and 22j at  $m/e$  91. The highest intensity peak at  $m/e$  105 (100) has been assigned to the benzoyl fragment 22i.

The mass spectral investigations of some of the cis-1,2-dibenzoylalkenes that we have examined, reveal that a general pathway for fragmentation is through the retro-Diels-Alder reaction, similar to that observed under thermal conditions. As is evident from Table I.3, the adducts 14, 16, 18, 20 and 22 gave rise to the appropriate diene or triene fragments in relatively high abundance. In the case of the adduct 15 also, a retro-Diels-Alder type of



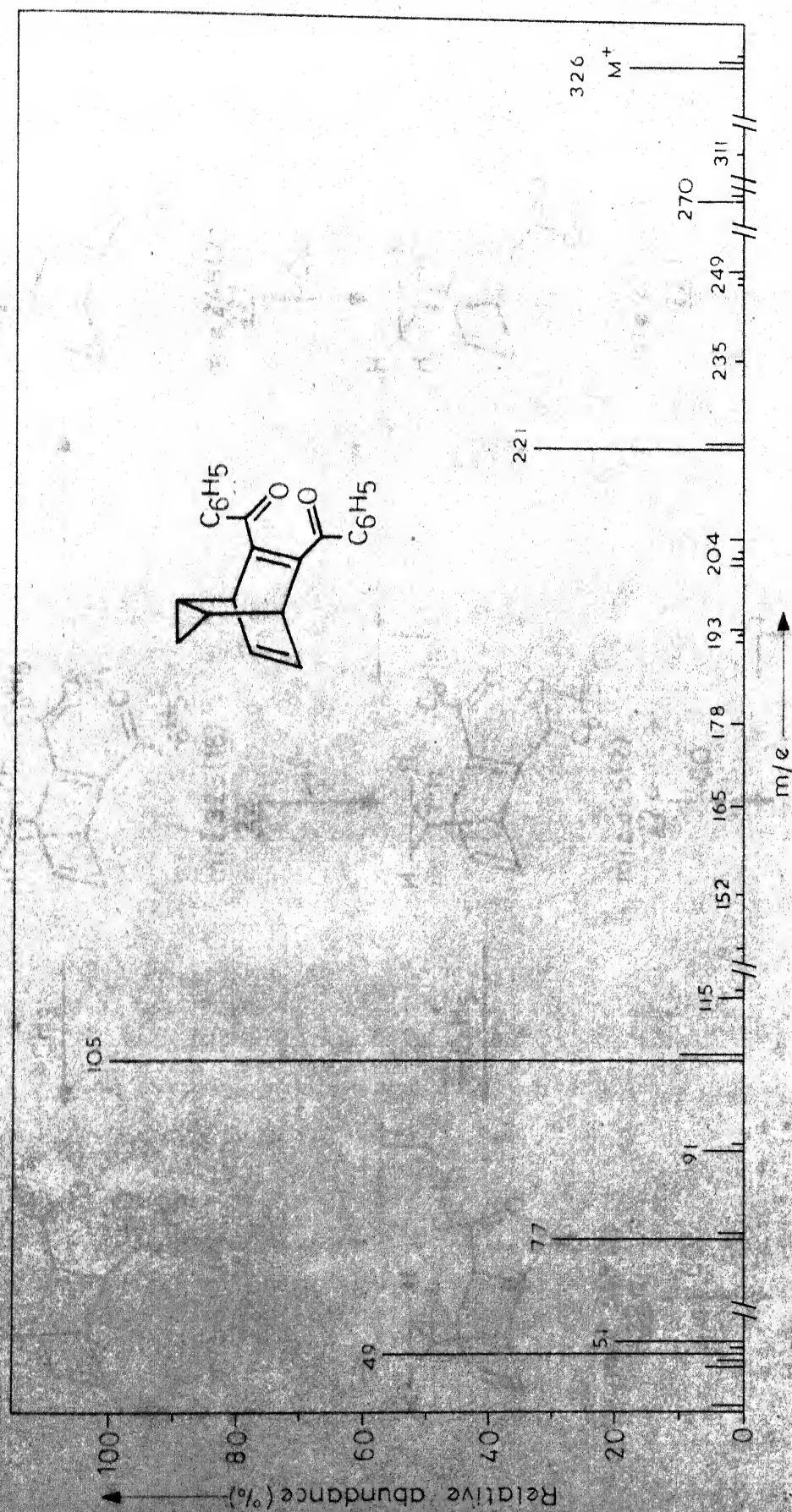
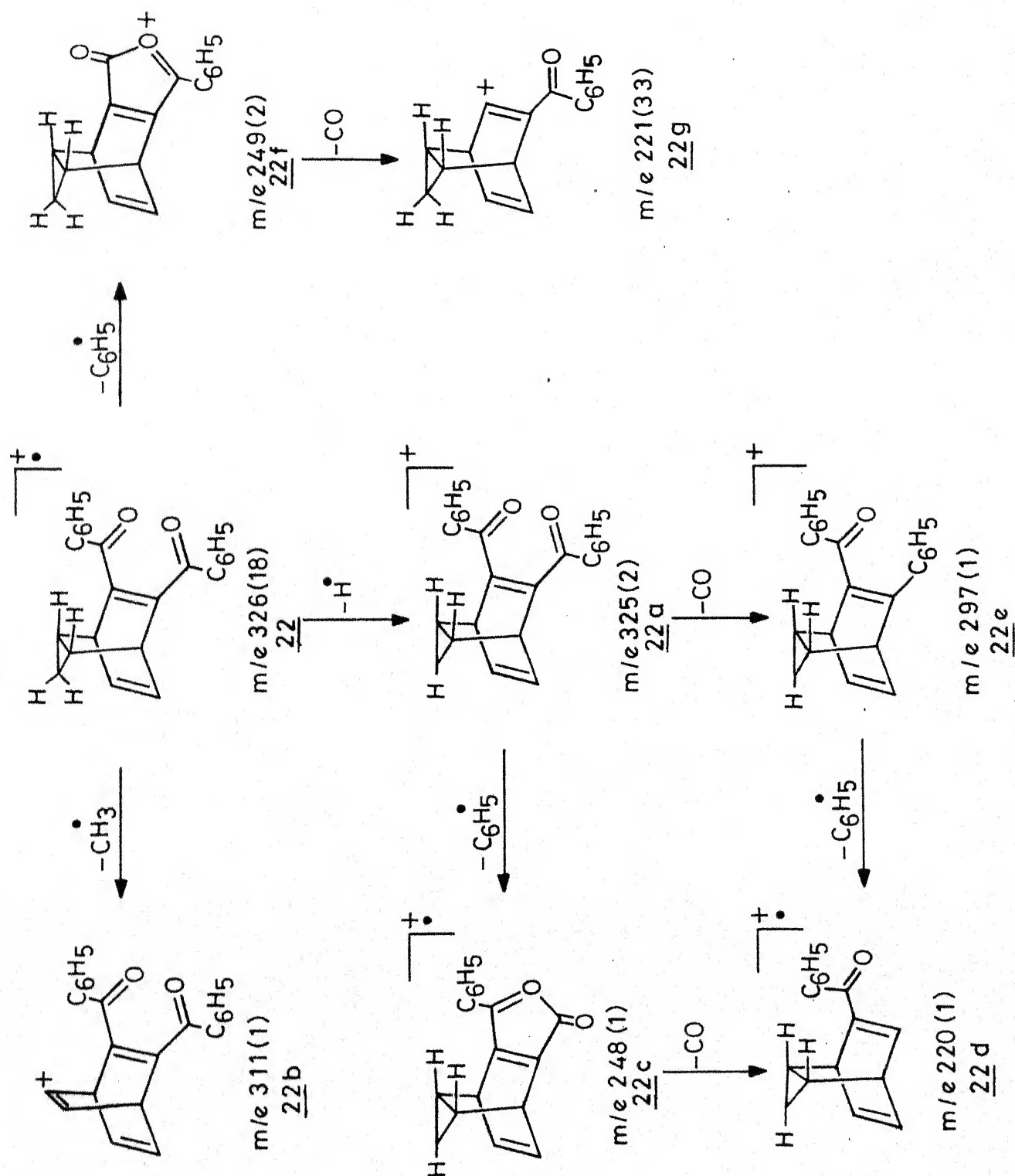
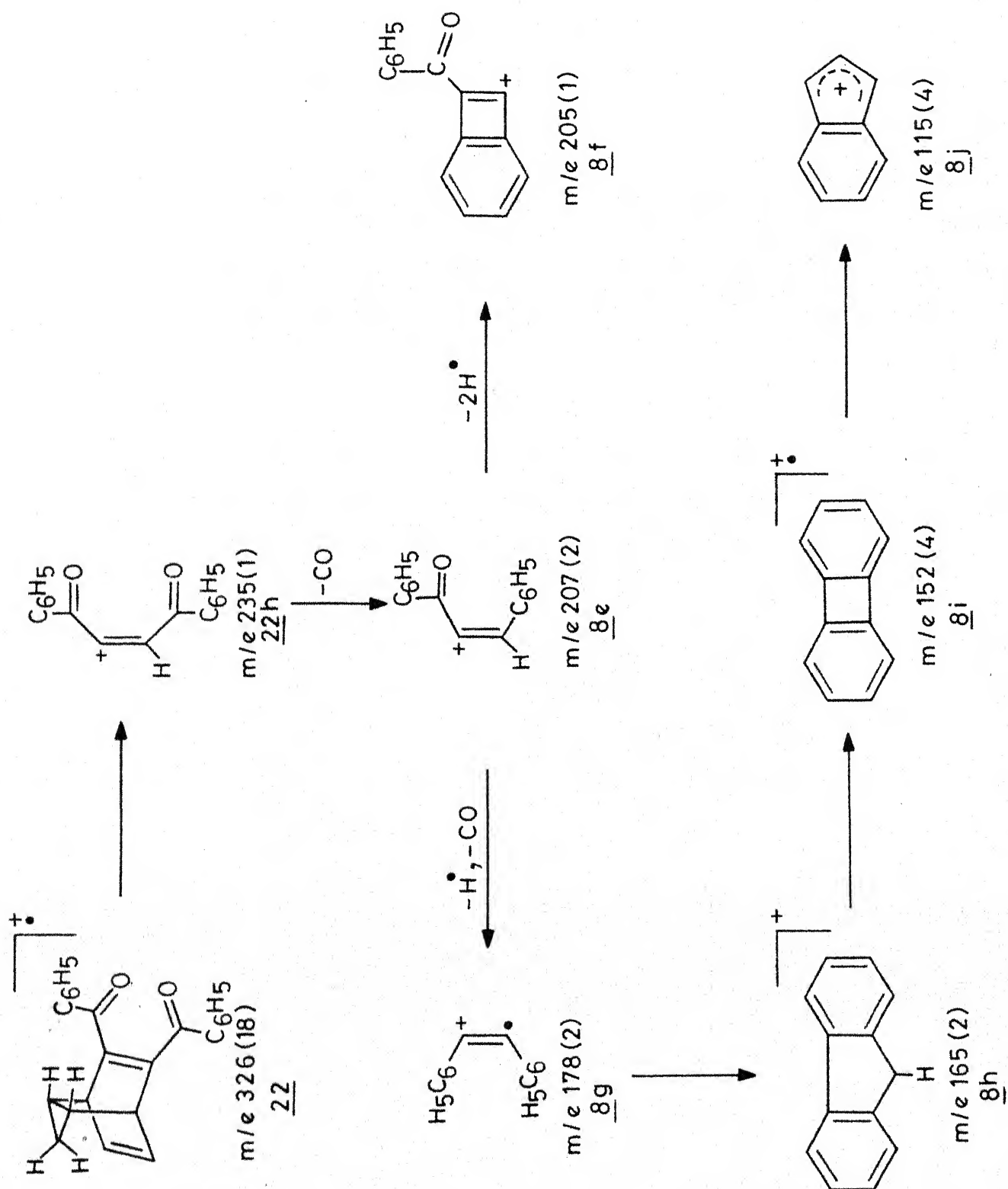


Fig. I. 16 Mass spectrum of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene(22)

Scheme 1.24



Scheme 1.24 (Contd)



Scheme 1.24 (Contd)

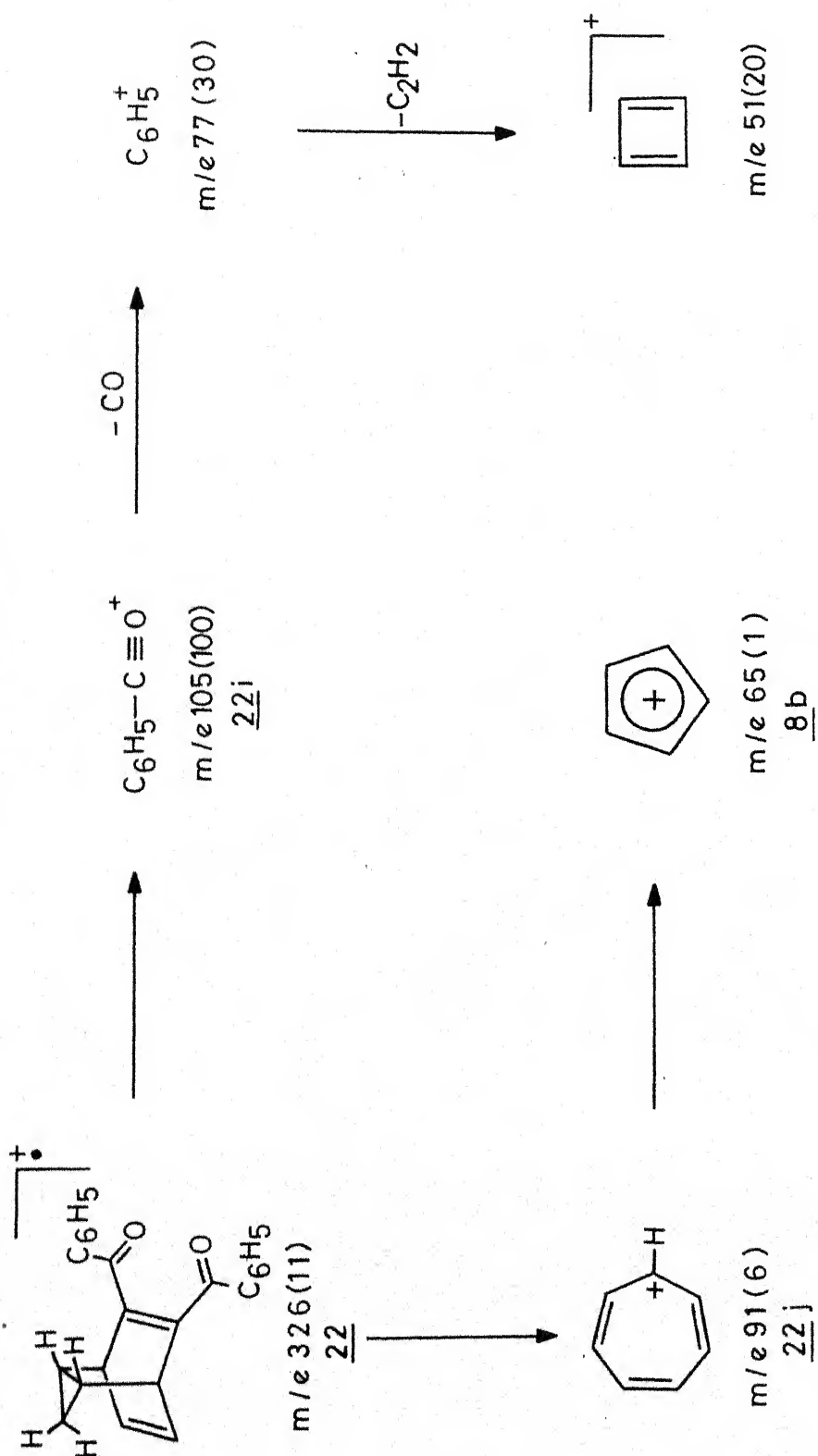


Table I.3 - Thermal and Electron Induced Fragmentation of cis-1,2-Dibenzoylalkenes




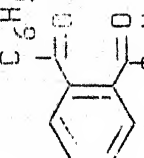
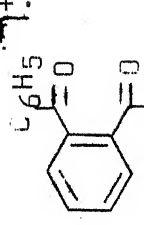

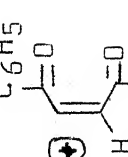
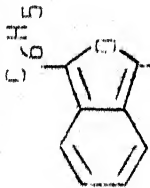
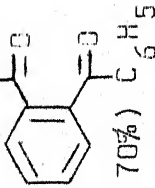
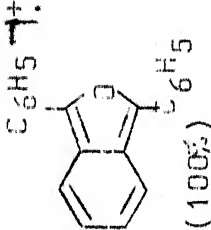
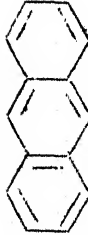
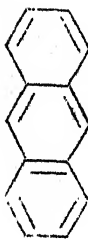
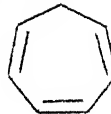
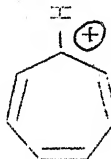
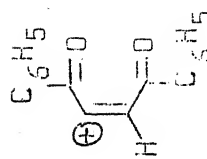
Adduct	Thermal Retro-Diels-Alder Reaction Products		Mass Spectral Retro-Diels-Alder Reaction fragments		Mass Spectral Retro-Diels-Alder Reaction with H transfer	
	Diene (%)	Dienophile (%)	Diene (Intensity %)	Dienophile (Intensity %)	Diene (Intensity %)	Dienophile (Intensity %)
1		3	4	5	6	7
2,3-Dibenzoyl-bicyclo 2.2.1-hepta-2,5-diene (14)		-		-	-	
	(62.5%)		(18%)			(12%)
2,3-Dibenzoyl-bicyclo-2.2.2-octa-2,5-diene (15)		-		-	-	-
	(99%)		(60%)			
7-Oxa-2,3-dibenzoylbicyclo 2.2.1-hepta-2,5-diene (16)	-	DBA (91%)		DBA (87%)	-	
			(31%)			(26%)

Table I.3 (...Contd.)

1	2	3	4	5	6	7
1,4-Diphenyl- 2,3-dibenzoyl- 1,4-epoxynaph- thalene (18)	 (2%) $\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5$  (70%) $\text{C}_6\text{H}_5$		 (100%) $\text{C}_6\text{H}_5$ DBA (15%)	-	-	-
9,10-Dihydro- 11,12-dibenzoyl- 9,10-etheno- anthracene (20)	 (83%)		 (65%)		-	-
6,7-Dibenzoyl- tricyclo- 3,2.2.0 <sup>2,4</sup> nona- 6,8-diene (22)			 (2%)		 (6%)	

fragmentation has been observed; but it proceeds with the loss of an ethylene moiety instead of dibenzoylacetylene. In some cases where there is a possibility for the retro-Diels-Alder reaction to proceed with hydrogen migration, as in the cases of 14, 16 and 22, such fragmentation modes have also been observed, as could be seen from Table I.3.

A second prominent mode of transformation of cis-1,2-dibenzoylalkenes involves the loss of CO from the molecular ions and it is reasonable to assume that this type of CO loss may be occurring from the rearranged 3-butenolides, in each case. It might be pointed out in this connection that similar rearrangements of the starting cis-1,2-dibenzoylalkenes have not been observed under thermal conditions, except in the case of cis-1,2-dibenzoylstilbene.

Table I.4 summarizes some of the major fragments, induced by electron-impact and their intensities. It is also apparent from Table I.4, that other fragmentation modes, like loss of phenyl and benzoyl groups from the molecular ions are also prominent in the case of most of the cis-1,2-dibenzoylalkenes that we have examined.

#### I.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. The ir spectra were

Table I.4. Some of the Fragments Formed under Electron Impact from cis-12-Dibenzoylalkenes and Their Intensities (%)

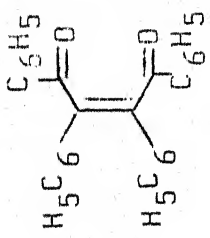
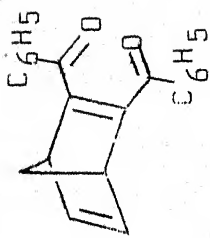
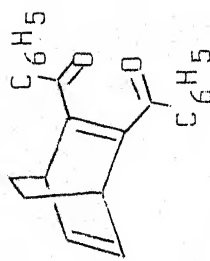
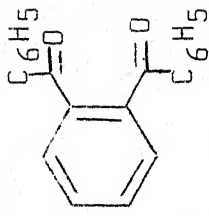
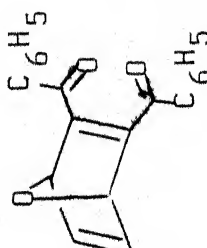
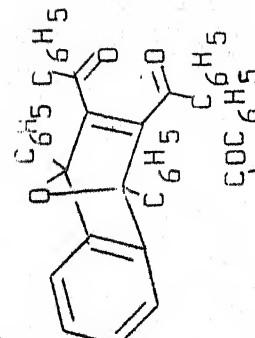
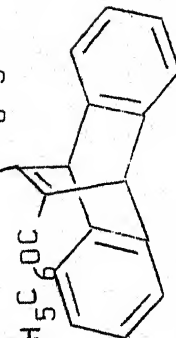
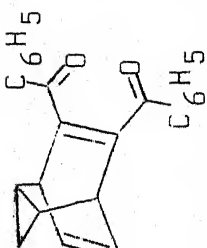
Nos.	Structure of the adduct	M <sup>+</sup>	[M-CO] <sup>+</sup>	[M-C <sub>6</sub> H <sub>5</sub> CO] <sup>+</sup>	[M-C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup>	m/e 178	m/e 165	m/e 152	C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>
1	2	3	4	5	6	7	8	9	10	11
<u>6</u>		28	5	26	6	60	14	8	100	98
<u>14</u>		100	5	21	4	3	10	5	38	38
<u>15</u>		67	could not be decided	could not be decided	-	1	2	10	50	25
<u>39</u>		32	3	6	100	-	4	30	37	37



Table I.4 (...Contd.)

1	2	3	4	5	6	7	8	9	10	11
<u>16</u>		15	6	13	-	34	1	4	100	65
<u>18</u>		5	-	9	-	5	5	-	35	15
<u>20</u>		83	-	27	-	could not be decided	-	-	100	21
<u>22</u>		18	-	33	2	2	2	1	100	30

recorded on Perkin-Elmer Model 137 or 521 Infrared Spectrometers. The electronic spectra were recorded on a Beckman DB spectrophotometer. Nmr traces were recorded on Varian A-60 or XL-100 NMR spectrometers using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E Single Focussing Mass Spectrometer or a Varian Mat CH7 Mass Spectrometer at 70 eV.

#### I.4.1 Starting Materials

Dibenzoylacetylene, mp 110-111°, was prepared by a reported procedure involving the bromination of trans-dibenzoylethylene,<sup>44</sup> followed by dehydrobromination of the dibromo derivative.<sup>45</sup> trans-Dibenzoylethylene itself was prepared by a reported procedure.<sup>46</sup> Cyclopentadiene, bp 41°, was freshly distilled before use and was obtained by the depolymerization of the 'Technical Grade' dicyclopentadiene. 1,3-Cyclohexadiene,<sup>47</sup> bp 79-80° and 1,3-diphenylisobenzofuran,<sup>48</sup> mp 130°, were prepared by reported procedures. cis-Dibenzoylstilbene, mp 216-17°, was prepared by the perbenzoic acid oxidation of tetraphenylfuran.<sup>49</sup>

#### I.4.2 Reaction of Cyclopentadiene with Dibenzoylacetylene

A mixture of cyclopentadiene (1.5 g, 0.02 mol) and dibenzoylacetylene (2.3 g, 0.01 mol) was refluxed in benzene (30 ml) for 3 hr. Removal of the solvent under vacuum and recrystallization of the residue from a mixture (2:1) of

petroleum ether (bp 60-80°) and benzene gave 2.9 g (98%) of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (14), mp 144° (lit.<sup>12</sup> mp 142-43°).

Anal. Calcd for  $C_{21}H_{16}O_2$ : C, 84.0; H, 5.33; Mol. wt., 300. Found: C, 84.25; H, 5.46; Mol. wt., 300 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3060, 3005 and 2983  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ , aromatic and olefinic), 2940 and 2875  $\text{cm}^{-1}$  ( $\nu_{\text{CH}_2}$ , asymmetric and symmetric), 1635  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1602 and 1575  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 258 nm ( $\epsilon$ , 16,200), 292 (6,600) and 349 (650).

In a repeat run, 3.2 g (0.014 mol) of dibenzoylacetylene was mixed with excess (15 ml) of cyclopentadiene and left at room temperature for 30 minutes. The reaction was exothermic and work-up of the mixture by removal of the unchanged cyclopentadiene under vacuum and fractional crystallization of the product from a mixture (1:1) of petroleum ether (bp 60-80°) and benzene gave 3.95 g (99%) of 14, mp 144° (mixture mp).

#### I.4.3 Reaction of 1,3-Cyclohexadiene with Dibenzoylacetylene

A mixture of dibenzoylacetylene (2.3g, 0.01 mol) and 1,3-cyclohexadiene (2g, 0.025 mol) in benzene (30 ml) was refluxed for 8 hr. Removal of the solvent under vacuum gave

a product which was recrystallized from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene to give 2.8 g (90%) of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (15), mp 153°.

Anal. Calcd for  $C_{22}H_{18}O_2$ : C, 84.07; H, 5.73; Mol. wt., 314. Found: C, 84.35; H, 5.62; Mol. wt., 314 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3080 and 3005  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 2935 and 2865  $\text{cm}^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric, 1640  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1605 and 1580  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 256 nm ( $\epsilon$ , 15,100), 287 (7,500) and 345 (400).

#### I.4.4 Reaction of Furan with Dibenzoylacetylene

A mixture of dibenzoylacetylene (0.6 g, 2.5 mmol) and furan (0.2 g, 2.5 mmol) was heated in a sealed tube around 50° for 9 hr. Removal of the unchanged furan gave a product which was chromatographed over silica-gel. Elution with a mixture (1:1) of petroleum ether (bp 60-80°) and benzene gave 0.1 g (17%) of dibenzoylacetylene, mp 111° (mixture mp).

Further elution of the column with a mixture (1:2) of petroleum ether (bp 60-80°) and benzene gave 0.3 g (46%) of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (16), mp 122-23°, after recrystallization from a mixture (1:1) of petroleum ether (bp 60-80°) and benzene.

Anal. Calcd for  $C_{20}H_{14}O_3$ : C, 79.9; H, 4.66; Mol. wt., 302. Found: C, 79.63; H, 4.48; Mol. wt., 302 (Mass Spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3265, 3105, 3055 and 3030  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1645  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1600 and 1580  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 256 nm ( $\epsilon$ , 13,000), 292 (5,900) and 344 (500).

In a repeat run a mixture of 2 g (8.5 mmol) of dibenzoylacetylene and excess (10 ml) of freshly distilled furan was heated in a sealed tube around 60–65° for 12 hr. Work-up of the mixture as in the earlier case gave 2 g (77%) of 16, mp 122–23° (mixture mp).

#### I.4.5 Reaction 1,3-Diphenylisobenzofuran with Dibenzoylacetylene

A mixture of dibenzoylacetylene (2.34g, 0.01 mol) and 1,3-diphenylisobenzofuran (2.7g, 0.01 mol) in benzene (50 ml) was refluxed for 8 hr. Removal of the solvent under vacuum gave a product which was treated with a small amount of hot ethanol. The solvent-insoluble portion was recrystallized from a mixture (2:1) of petroleum ether and cyclohexane to give 200 mg (6%) of a product, mp 250°, identified as 9,10-diphenylanthracene (lit.<sup>50</sup> mp 249–50°).

Anal. Calcd for  $C_{26}H_{18}$ : C, 94.54; H, 5.45; Mol. wt., 330. Found: C, 94.40; H, 5.51; Mol. wt., 330 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3065 and 3030  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1598  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Cyclohexane)  $\lambda_{\max}$ : 221 nm ( $\epsilon$ , 24,000), 261 (114,800) and 375 (13,200).

Nmr spectrum ( $\text{CDCl}_3$ ): 7.6 $\delta$  (aromatic protons).

Mass spectrum  $m/e$  (rel. intensity): 330(100), 329(12), 328(10), 327(9), 253(14), 252(25), 163(4), 162(3), 156(4), 150(4), 138(2), 137(2), 126(2) and 77(22).

Concentration of the alcohol soluble portion and fractional crystallization from ethanol gave 3.6 g (71%) of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18), mp 157°.

Anal. Calcd for  $\text{C}_{36}\text{H}_{24}\text{O}_3$ : C, 85.70; H, 4.76; Mol. wt., 504. Found: C, 85.90; H, 4.35; Mol. wt., 504 (Mass Spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3055 and 3025  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1657  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1601, 1581 and 1500  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 258 nm ( $\epsilon$ , 14,000), 284 (5,500) and 348 (250).

Nmr spectrum ( $\text{CDCl}_3$ ): 7.5 $\delta$  (multiplet, aromatic).

#### I.4.6 Reaction of 1,3-Diphenylisobenzofuran with Benzene

A sample of 1,3-diphenylisobenzofuran (100 mg, 0.37 mmol) was refluxed in 20 ml of benzene for 24 hr under

nitrogen atmosphere. The solvent was removed under vacuum and the residue was chromatographed over silica-gel. Elution with petroleum ether (bp 60-80°) gave 0.8 g (1%) of 9,10-diphenylanthracene, mp 250° (mixture mp).

Further elution of the column with a mixture (10:1) of petroleum ether (bp 60-80°) and benzene, gave 25 mg (25%) of the starting material, mp 131° (mixture mp).

Subsequent elution of the column with a mixture (1:1) of petroleum ether (bp 60-80°) and benzene gave 4 mg (4%) of 1,2-dibenzoylbenzene, mp 149-150° (mixture mp).

#### I.4.7. Reaction of Anthracene with Dibenzoylacetylene

Heating a mixture of dibenzoylacetylene (2.34 g, 0.01 mol) and anthracene (1.78 g, 0.01 mol) around 200° in a sealed tube for 30 minutes and work-up of the mixture by fractional crystallization from xylene gave 2.5 g (60%) of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20), mp 212° (lit.<sup>17a</sup> mp 212-215.5°).

Ir spectrum (KBr)  $\nu_{\max}$ : 3225  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1670  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1620 and 1590  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 262 nm ( $\epsilon$ , 15,000), 295 (5,600) and 345 (1,400).

Nmr spectrum ( $\text{CDCl}_3$ ): 5.66 $\delta$  (singlet, 2H, bridgehead) and 7.25 $\delta$  (multiplet, 14H, aromatic).

#### I.4.8 Reaction of Cycloheptatriene with Dibenzoylacetylene

##### A In Toluene

A mixture of dibenzoylacetylene (2.3 g, 0.01 mol) and cycloheptatriene (2 g, 0.02 mol) was refluxed in toluene (50 ml) for 20 hr. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with a mixture (1:1) of petroleum ether (bp 60-80°) and benzene gave 590 mg (18%) of 6,7-dibenzoyltricyclo-[3.2.2.0<sup>2,4</sup>] nona-6,8-diene (22) mp 133°, after recrystallization from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene.

Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: C, 84.66; H, 5.52; Mol. wt., 326. Found: C, 84.84; H, 6.08; Mol. wt., 326 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3283 cm<sup>-1</sup> ( $\nu_{\text{C-H}}$ , cyclopropyl), 3060, 3005 and 2980 cm<sup>-1</sup> ( $\nu_{\text{C-H}}$ ), 1645 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ), 1595 and 1580 cm<sup>-1</sup> ( $\nu_{\text{C=C}}$ ), 1038 cm<sup>-1</sup> (CH<sub>2</sub>, wagging).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 255 nm ( $\epsilon$ , 13,500), 290 (6,300) and 350 (500).

Further elution of the column with benzene gave 70 mg (2%) of 3,4-dibenzoylbicyclo[3.2.2] nona-2,6,8-triene (23), mp 156°, after recrystallization from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene.



Anal. Calcd for  $C_{23}H_{18}O_2$ : C, 84.66; H, 5.52; Mol. wt., 326. Found: C, 84.66; H, 5.83; Mol. wt., 326 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3220, 3150 and 3060  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 1680 and 1660  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1600 and 1585  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 250 nm ( $\epsilon$ , 20,000), 274 (8,700) and 320 (400).

#### B In the Absence of Any Solvent

A mixture of 4.68 g (0.02 mol) of dibenzoylacetylene and excess (10 ml) of cycloheptatriene was heated in a sealed tube around 95-100° for 16 hr. The reaction mixture was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 1.8 g (28%) of 22, mp 133° (mixture mp), after recrystallization from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene.

Further elution of the column with a mixture (20:1) of petroleum ether (bp 60-80°) and benzene gave 15 mg (0.3%) of 23, mp 156° (mixture mp), after recrystallization from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene.

Subsequent elution with a mixture (10:1) of petroleum ether (bp 60-80°) and benzene gave 30 mg (0.6%) of an unidentified yellow solid (25), mp 181°, after recrystallization from a mixture (1:1) of chloroform and petroleum ether (bp 60-80°).

Anal. Calcd for  $C_{32}H_{20}O_4$ : C, 82.05; H, 4.27; Mol. wt., 468. Found: C, 81.53; H, 4.36; Mol. wt., 468 (Mass Spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3205, 3185 and 3065  $cm^{-1}$  ( $\nu_{C-H}$ ), 1655  $cm^{-1}$  ( $\nu_{C=O}$ ), 1638, 1630 and 1590  $cm^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 255 nm ( $\epsilon$ , 40,000), 288 (18,200) and 328 (12,600).

Nmr spectrum ( $CDCl_3$ ): 7.43 $\delta$  (multiplet, 16H, aromatic) and 8.33 $\delta$  (multiplet, 4H, aromatic).

Mass spectrum m/e (rel. intensity): 468(100), 451(14), 392(12), 391(43), 363(7), 313(8), 305(4), 276(4), 234(3), 229(2), 105(16), 92(6), 91(10), 78(45) and 77(18).

Continued elution of the column with the same solvent mixture gave 70 mg (1.5%) of a second yellow solid, 24, mp 206°, after recrystallization from a mixture (1:1) of chloroform and petroleum ether(bp 60-80°).

Anal. Calcd for  $C_{32}H_{20}O_4$ : C, 82.05; H, 4.27; Mol. wt., 468. Found: C, 81.72; H, 4.45; Mol. wt., 468 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3455  $cm^{-1}$  ( $\nu_{O-H}$ ), 3195, 3055 and 2915  $cm^{-1}$  ( $\nu_{C-H}$ ), 1670 and 1655  $cm^{-1}$  ( $\nu_{C=O}$ ), 1630 and 1590  $cm^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 254 nm ( $\epsilon$ , 43,600), 287 (20,000) and 326 (14,000).

Nmr spectrum ( $\text{CDCl}_3$ ): 4.16 $\delta$  (singlet, 1H, -OH), 7.46 $\delta$  (multiplet, 15H, aromatic) and 8.26 $\delta$  (multiplet, 4H, aromatic).

Mass spectrum m/e (rel. intensity): 468(100), 451(9), 392(10), 391(35), 363(6), 313(8), 305(2), 289(2), 285(1), 276(3), 234(2), 229(2), 105(15), 92(5), 91(10), 78(43) and 77(17).

#### I.4.9 Thermolysis of cis-Dibenzoylstilbene (6)

A sample of cis-dibenzoylstilbene (6) (60 mg, 0.15 mmol) was heated around 260° for 30 minutes. The reaction mixture was fractionally crystallized from ethanol to give 55 mg (92%) of 2,2,3,4-tetraphenylbut-3-enolide (9), mp 137-38° (mixture mp).

In a repeat run, 200 mg (0.51 mmol) of 6 was refluxed in 30 ml of nitrobenzene for 20 hr. Removal of the solvent under vacuum and work-up of the mixture as in the earlier case gave 125 mg (96%) of 9, mp 138° (mixture mp).

#### I.4.10 Thermolysis of 2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (14)

A 500 mg (1.67 mmol) sample of 2,3-dibenzoylbicyclo-[2.2.1] hepta-2,5-diene (14) was heated around 160° in a sealed tube under vacuum for 4 hr. After cooling, the sealed tube was broken and the clear liquid that was collected in the upper portion of the tube was removed to give

33 mg (30%, 63% on the basis of reacted starting material) of cyclopentadiene, identified through a comparison of its ir spectrum and glc retention time, with those of an authentic sample.

The dark residual mass left in the tube was fractionally crystallized from a mixture (2:1) of petroleum ether (bp 60-80°) and benzene to give 200 mg (40%) of the unchanged starting material, mp 144° (mixture mp). No other product could be isolated from this run.

In a repeat run, 190 mg (0.63 mmol) of 14 was heated around 200° in an open tube for 2 hr. Colourless droplets of cyclopentadiene was collected in the cooler parts of the tube. On continued heating for 12 hr, a small amount (15 mg, 19%) of benzoic acid, mp 121° (mixture mp) was isolated from the cooler parts of the tube. Work-up of the residual brown mass in the reaction tube did not give rise to any isolable product.

#### I.4.11 Thermolysis of 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (15)

A sample of 2,3-dibenzoylbicyclo[2.2.2] octa-2,5-diene (15) (0.4 g, 1.2 mmol) was heated in a sealed tube around 160° for 2 hr. The product mixture was crystallized from a mixture (1:2) of acetone and ethanol to give 0.36 g (99%) of 1,2-dibenzoylbenzene (39), mp 150° (mixture mp).

I.4.12 Attempted Thermolysis of 1,2-Dibenzoylbenzene (39)

A sample of 1,2-dibenzoylbenzene (39) (150 mg, 0.52 mmol) was heated in a sealed tube around 250° for 6 hr. Work-up of the mixture in the usual manner and crystallization of the product from a mixture (1:1) of petroleum ether (bp 60-80°) and benzene gave 145 mg (97%) of the unchanged starting material, mp 149-50° (mixture mp).

I.4.13 Thermolysis of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]-hepta-2,5-diene (16)

A solution of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (16) (100 mg, 0.32 mmol) in dioxan (20 ml) was refluxed for 4 hr. Removal of the solvent under vacuum gave a solid mass which was treated with water and then was extracted with chloroform. Work-up of the chloroform extract in the usual manner gave 70 mg (90%) of dibenzoylacetylene, mp 110° (mixture mp), after recrystallization from cyclohexane.

I.4.14 Thermolysis of 1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18)

A solution of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene (18) (250 mg, 0.5 mmol) in diphenyl ether (20 ml) was refluxed for 12 hr. Removal of the solvent under vacuum gave a product mixture which was chromatographed over silica-gel.

Elution of the column with a mixture (10:1) of petroleum ether (bp 60-80°) and benzene gave 2 mg (2%, 2.5% on the basis of the reacted starting material) of 1,3-diphenylisobenzofuran, mp 130° (mixture mp).

Further elution of the column with a mixture (5:1) of petroleum ether (bp 60-80°) and benzene gave 100 mg (40%) of the starting material, mp 156-57° (mixture mp).

Subsequent elution with 1:1 mixture of petroleum ether (bp 60-80°) and benzene gave 60 mg (42%, 71% on the basis of the reacted starting material) of 1,2-dibenzoylbenzene (39), mp 149-50° (mixture mp).

#### I.4.15 Thermolysis of 1,3-Diphenylisobenzofuran (17)

A solution of 1,3-diphenylisobenzofuran (17) (54 mg, 0.2 mmol) in diphenylether (15 ml) was refluxed for 18 hr. Removal of the solvent under vacuum gave a product which was fractionally crystallized from a mixture (1:1) of petroleum ether (bp 60-80°) and benzene to give 42 mg (73%) of 1,2-dibenzoylbenzene (39), mp 149-50° (mixture mp).

#### I.4.16 Thermolysis of 9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20)

A sample of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (20) (200 mg, 0.5 mmol) was thermolyzed around 260° for 2 hr in a sealed tube. The thermolyzed product was chromatographed over alumina. Elution with petroleum ether

(bp 60-80°) gave 50 mg (58%, 83% on the basis of the reacted starting material) of anthracene, mp 215° (mixture mp).

Further elution of the column with a mixture of (20:1) of petroleum ether (bp 60-80°) and benzene gave 60 mg (30%) of the unchanged starting material, mp 212° (mixture mp).

I.4.17 Reaction of 9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene with Phosphorus Pentasulphide

A mixture of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (1.03 g, 2.5 mmol) and phosphorous pentasulphide (1.11 g, 5 mmol) was refluxed in o-xylene (50 ml) for 1 hr. Removal of the solvent under vacuum gave a product which was treated with a 5% solution of sodium hydroxide and subsequently extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product which was chromatographed over neutral alumina.

Elution with petroleum ether (bp 60-80°) gave 0.8 g of a mixture of products consisting of 12,14-diphenyl-9,10(3',4')-furanoanthracene (44) and 12,14-diphenyl-9,10(3',4')thiophenoanthracene (47), mp 215-220°.

The mixture consisting of 44 and 47 (0.8 g) was treated with 0.2 g (2 mmol) of maleic anhydride in dry benzene (20 ml) and the solution was allowed to stand at room temperature for 3 hr. Removal of the solvent under reduced pressure gave a product-mixture which was

recrystallized from cyclohexane. The recrystallized product appeared to be a mixture of two crystalline products. The colourless crystals from this mixture were hand-separated and was subsequently chromatographed over alumina. Elution of the column with petroleum ether (bp 60-80°) gave 0.2 g (20%) of 12,14-diphenyl-9,10(3',4')-furanoanthracene (44), mp 217-18°, after recrystallization from a mixture (1:2) of petroleum ether (bp 60-80°) and benzene.

Anal. Calcd for  $C_{30}H_{20}O$ : C, 90.91; H, 5.05; Mol. wt., 396. Found: C, 90.63; H, 5.18; Mol. wt., 396 (Mass Spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3020, 3000 and 2980  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 1602 and 1490  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (cyclohexane)  $\lambda_{\max}$ : 250 nm ( $\epsilon$ , 15,050) and 312 (20,900).

Nmr spectrum ( $CDCl_3$ ): 5.65 $\delta$  (singlet, 2H, bridgehead) and 7.37 $\delta$  (multiplet, 14H, aromatic).

Removal of the colourless crystals of maleic anhydride adduct, left behind 0.45 g (44.5%) of a crystalline material which appeared to be a 1:1 mixture of 12,14-diphenyl-9,10(3',4') furanoanthracene and 12,14-diphenyl-9,10(3',4')-thiophenoanthracene, mp 226-228°.



Anal. Calcd for  $C_{60}H_{40}OS$ : C, 89.11; H, 4.95.  
Found: C, 89.05, H, 5.07.

Ir spectrum (KBr)  $\nu_{\max}$ : 3030, 3005 and 2985  $\text{cm}^{-1}$   
( $\nu_{C-H}$ ), 1605, 1580 and 1494  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (cyclohexane)  $\lambda_{\max}$ : 250 nm ( $\epsilon$ , 20,410)  
and 324 (31,090).

Nmr spectrum ( $CDCl_3$ ): 5.53 $\delta$  (singlet, 2H, bridgehead  
protons of thiophenoanthracene), 5.63 $\delta$  (singlet, 2H, bridge-  
head protons of furanoanthracene) and 7.37 $\delta$  (multiplet, 36H,  
aromatic).

Mass spectrum: m/e 412(100), 396(51), 379(21), 376(51),  
335(10), 334(10), 302(11), 292(7), 291(36), 290(10), 289(26),  
287(7), 263(4), 189(9), 188(4), 178(7), 167(6), 121(48),  
105(35) and 77(7).

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## CHAPTER II

### PHOTOCHEMICAL TRANSFORMATIONS OF cis-1,2-DIBENZOYLALKENES

#### II.1 ABSTRACT

Photolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (18) in benzene solution gave a 90% yield of 2,3-dibenzoylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (19), through an intramolecular cycloaddition process. The photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (20) under similar conditions, on the other hand, gave a mixture of products consisting of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylic acid (21) (26%), 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]-oct-2-ene-5-endo-carboxylic acid (22) (6%) and a lactone,

23 (23%). However, when the photolysis of 20 was carried out in methanol, the products formed were the methyl esters of 21 and 22 in 69% and 1% yields, respectively. In the photolysis of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (36), the only product that could be isolated was an isomeric lactone (38) (33%) which was analogous to the lactone 23, obtained in the photolysis of 20. The photochemical transformation of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (46) gave a mixture of products consisting of 1,5-dibenzoyl-5-formyl-1,3-cyclopentadiene (49) (32%) and dibenzoylacetylene (13%). The photolysis of 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (60), on the other hand, gave a 88% yield of 1,2-dibenzoyl-dibenzotricyclo[3.3.0.0<sup>2,8</sup>]octadiene (63), formed through a di- $\pi$ -methane rearrangement.

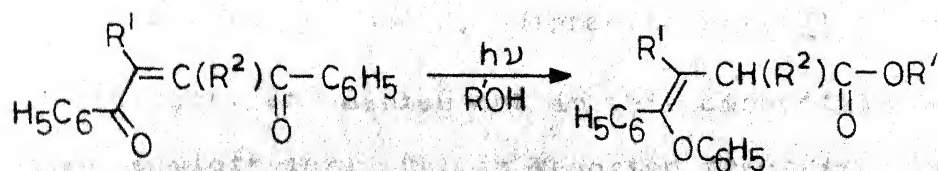
The structures of all the photoproducts have been established on the basis of analytical results and spectral data. Reasonable mechanisms for the formation of different products in these photochemical reactions have been suggested.

## II.2 INTRODUCTION

Photochemical transformations of  $\alpha,\beta$ -unsaturated carbonyl compounds have been extensively studied in recent

years, by several group of workers. Mention may be made in this connection of the detailed investigations on the photo-transformations of dibenzoylethylenes. It has been shown by Griffin and O'Connell<sup>1</sup> and also by Zimmerman and coworkers<sup>2</sup> that dibenzoylethylenes (1) undergo an interesting photorearrangement in protic solvents, leading to the formation of esters (2). Thus, it has been observed that the photolysis of dibenzoylethylene (1a) in ethanol leads to the formation of ethyl 4-phenyl-4-phenoxy-3-butenate (2a). Similar transformations have been observed in the case of both dibenzoylstyrene (1b) and dibenzoylstilbene (1c) and leading to the formation of the corresponding esters, 2b and 2c, respectively (Scheme II.1).<sup>3</sup> In a recent investigation, Padwa and coworkers<sup>4</sup> have shown that the photolysis of trans-dibenzoylstilbene (3c) gives rise to different products, depending on the nature of the solvent employed. Thus, the photolysis of 3c in benzene, for example, gave a mixture of products consisting of cis-dibenzoylstilbene (1c) and 1-hydroxy-2,3-diphenyl-4-phoxynaphthalene (4), whereas 2,3,4-triphenyl-4-phenoxy-3-butenic acid (5), was formed in aqueous dioxan (Scheme II.2). Similarly, Sugiyama and Kashima<sup>5</sup> have observed that the photolysis of dibenzoylethylene (1a) in acidic methanol results in the formation of a mixture of products consisting of

Scheme II.1



1 a)  $\text{R}' = \text{R}^2 = \text{H}$

b)  $\text{R}' = \text{H}; \text{R}^2 = \text{C}_6\text{H}_5$

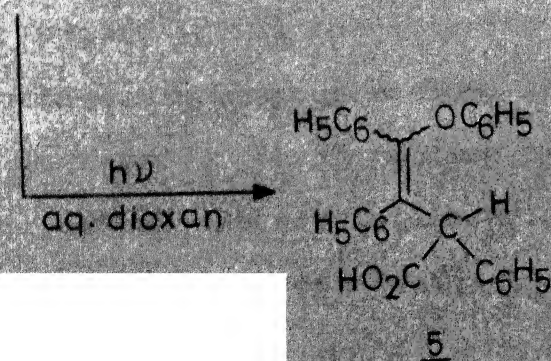
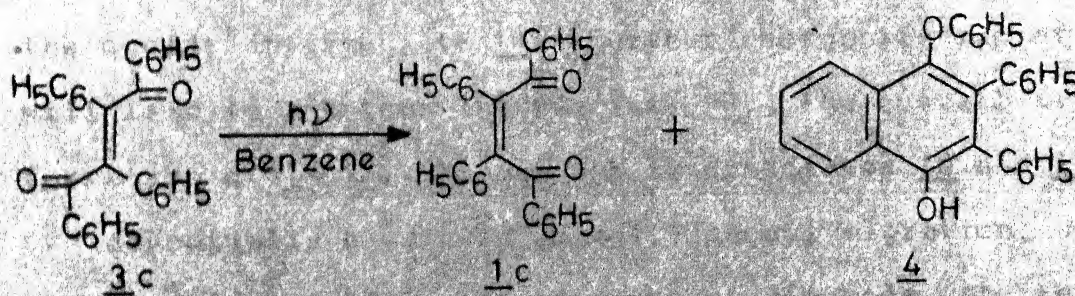
c)  $\text{R}' = \text{R}^2 = \text{C}_6\text{H}_5$

2 a)  $\text{R}' = \text{R}^2 = \text{H}; \text{R}' = \text{C}_2\text{H}_5$

b)  $\text{R}' = \text{H}; \text{R}^2 = \text{C}_6\text{H}_5; \text{R}' = \text{C}_2\text{H}_5$

c)  $\text{R}' = \text{R}^2 = \text{C}_6\text{H}_5; \text{R}' = \text{CH}_3$

Scheme II.2



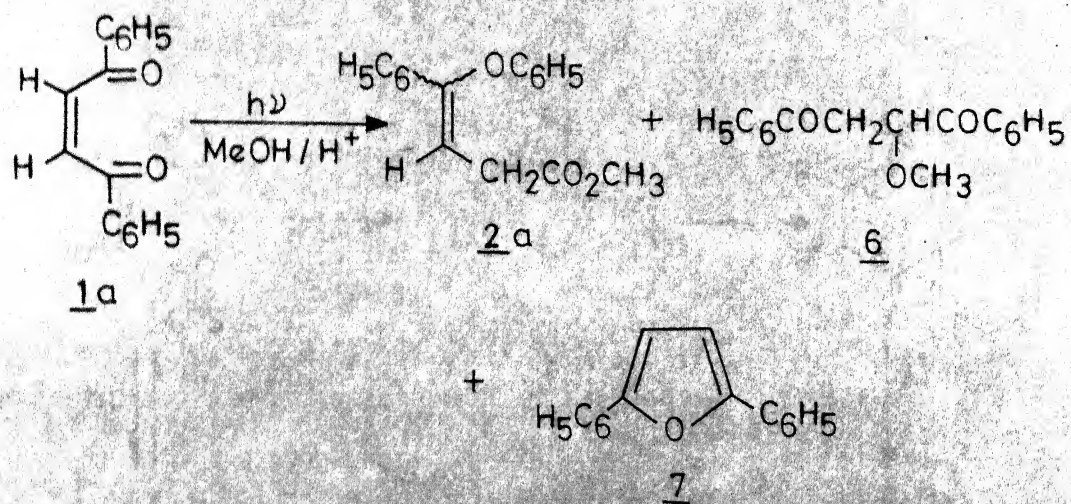


methyl 4-phenyl-4-phenoxy-3-butenolate (2a), 1,2-dibenzoyl-1-methoxyethane (6) and 2,5-diphenylfuran (7) (Scheme II.3).

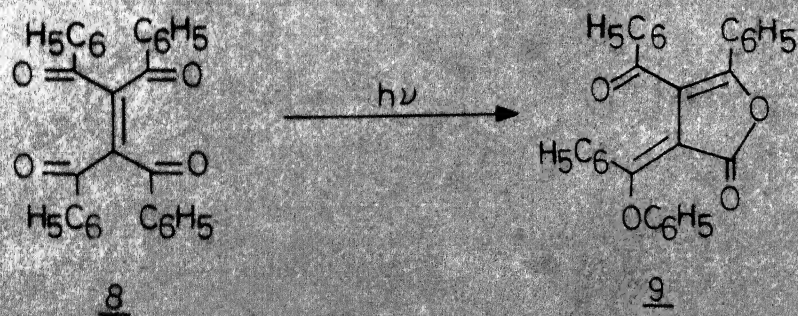
It might be pointed out in this connection that tetrabenzoylethylene (8) is reported to undergo isomerization to the lactone, 9 under photochemical conditions (Scheme II.4).<sup>6</sup>

Zimmerman and coworkers<sup>2,3</sup> have suggested that the photo-transformations of dibenzoylethylenes (1) to the corresponding esters (2) can be rationalized in terms of a pathway shown in Scheme II.5. They have assumed that the initial step in the reaction of 1 involves an  $n-\pi^*$  excitation of one of the carbonyl groups to give the diradical intermediate 10, which can subsequently interact with the  $\pi$ -system of an adjacent aromatic nucleus to give the cyclic intermediate 11. Further reorganization of 11 will lead to a ketene intermediate, 12. The overall transformation of 1  $\rightarrow$  12, through the intermediates 10 and 11 can essentially be viewed as a [1,5]phenyl migration, as shown in Scheme II.5. In presence of alcohols, the ketene intermediate 12, is converted to the corresponding ester 2, whereas, in aqueous medium, the corresponding carboxylic acid is formed. The formation of the phenol, 4 in the photolysis of dibenzoylstilbene (1c) has been rationalized in terms of the intermediates 13 and 14, resulting from

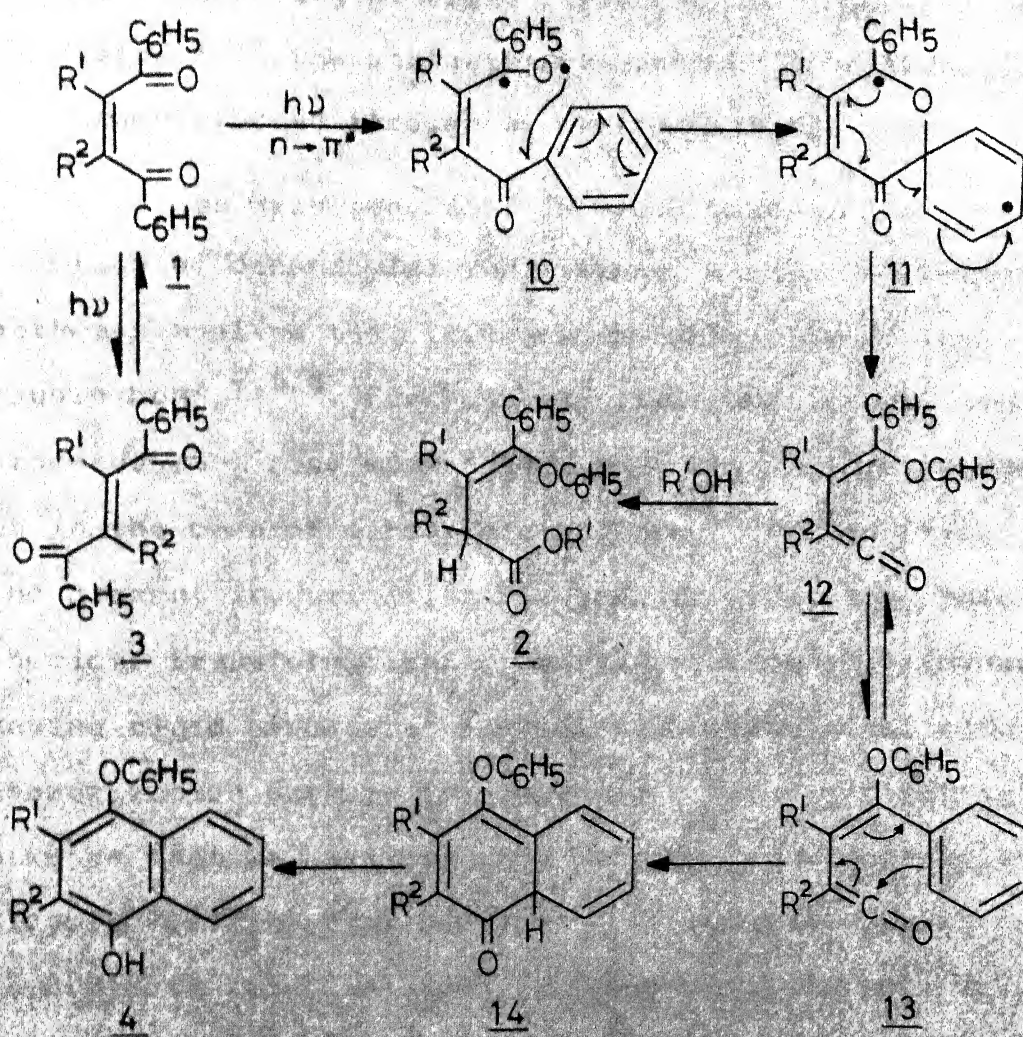
Scheme II.3



Scheme II.4



Scheme II.5



further isomerisation of the ketene intermediate 12, as shown in Scheme II.5. The poor yields of the rearranged products from trans-dibenzoylalkenes, as observed by Zimmerman and coworkers,<sup>3</sup> support the cis-stereochemical requirement of the proposed mechanism. On the basis of detailed quenching studies, Zimmerman and coworkers have suggested that the photo-transformations of dibenzoyl-ethylenes proceed through an excited singlet state.<sup>3,7</sup>

It has been generally observed that in the photo-reaction of dibenzoylalkene systems, a major photochemical pathway involves the cis-trans isomerization of the alkene double bond.<sup>4,5,8</sup> Further, the cis-trans isomerization proceeds at a rate much faster than the photorearrangement, as in the case of dibenzoylethylenes.<sup>2-4</sup> The object of the present investigation has been to study the photochemical transformations of a few cis-dibenzoylalkenes, having rigid structural features and wherein the cis-trans isomerization pathway is prevented. The cis-dibenzoylalkenes that we have examined include, 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (18), 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (20), 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]-nona-6,8-diene (37), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (47) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (60).

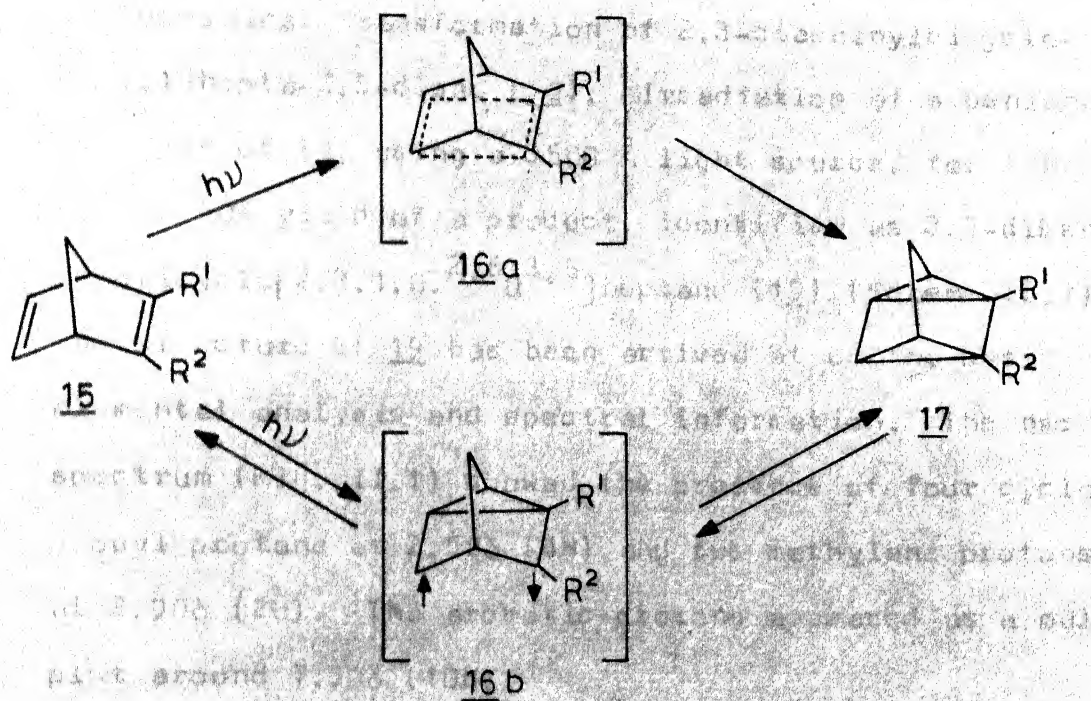
## II.3 RESULTS AND DISCUSSIONS

### II.3.1 Photo-transformation of 2,3-Dibenzoylbicyclo- [2.2.1]hepta-2,5-diene

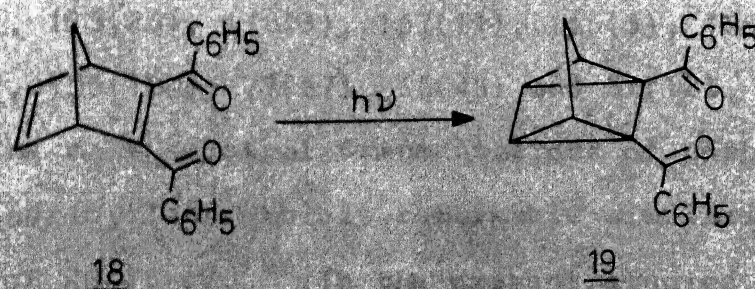
Cristol and Snell in 1958, have shown that norbornadiene derivatives undergo photochemical transformations, leading to the formation of quadricyclanes.<sup>9</sup> Since then, several such intramolecular photo-cycloaddition reactions have been studied in great detail.<sup>10-15</sup> In general, the photo-transformation of norbornadienes (15) can proceed through either a symmetry allowed,  $[\pi^2s + \pi^2s]$  process or through a diradical pathway, as shown in Scheme II.6. It has been shown that the photochemical conversion of norbornadienes (15) to quadricyclanes (17) can be brought about both under direct and sensitized excitation conditions. The quadricyclanes themselves are relatively stable compounds and their thermal stability is attributed to the symmetry-forbidden pathway that is involved in the ring-opening process ( $2\sigma \rightarrow 2\pi$ ), which will lead to the starting materials.<sup>13</sup> It has been observed that, in general, the structural distortions of the norbornadiene skeleton due to different substituents have practically very little influence on the photochemical addition pathway. Also, it has been shown, on the basis of quantum yield studies and quenching experiments, that



### Scheme II.6



### Scheme II.7



the photochemical transformation of norbornadienes to quadricyclanes occur through the singlet excited states.<sup>14</sup>

In the present investigation, we have examined the photochemical transformation of 2,3-dibenzoylbicyclo-[2.2.1]hepta-2,5-diene (18). Irradiation of a benzene solution of 18, using a 3500 Å light source, for 1 hr gave a 90% yield of a product, identified as 2,3-dibenzoyl-quadricyclo[2.2.1.0.<sup>2,6</sup>0<sup>3,5</sup>]heptane (19) (Scheme II.7). The structure of 19 has been arrived at on the basis of elemental analysis and spectral information. The nmr spectrum (Fig. II.1) showed the presence of four cyclopropyl protons at 2.58δ (4H) and two methylene protons at 2.90δ (2H). The aromatic protons appeared as a multiplet around 7.30δ (10H).

Further proof for the structure of 19 was derived from its mass spectrum. The mass spectrum of 19 (Fig. II.2) showed a molecular ion peak at m/e 300 (36). Other peaks in the spectrum were observed at m/e 235(8), 223(4), 207(5), 195(26), 178(3), 167(11), 166(3), 165(9), 152(4), 115(4), 105(100), 77(67), 66(45) and 51(12). It is known that the mass spectral fragmentations of norbornadiene and quadricyclane exhibit remarkable similarity in the range of 20-75 eV.<sup>16</sup> In the present studies, we find that the mass spectral fragmentations of 19 are very

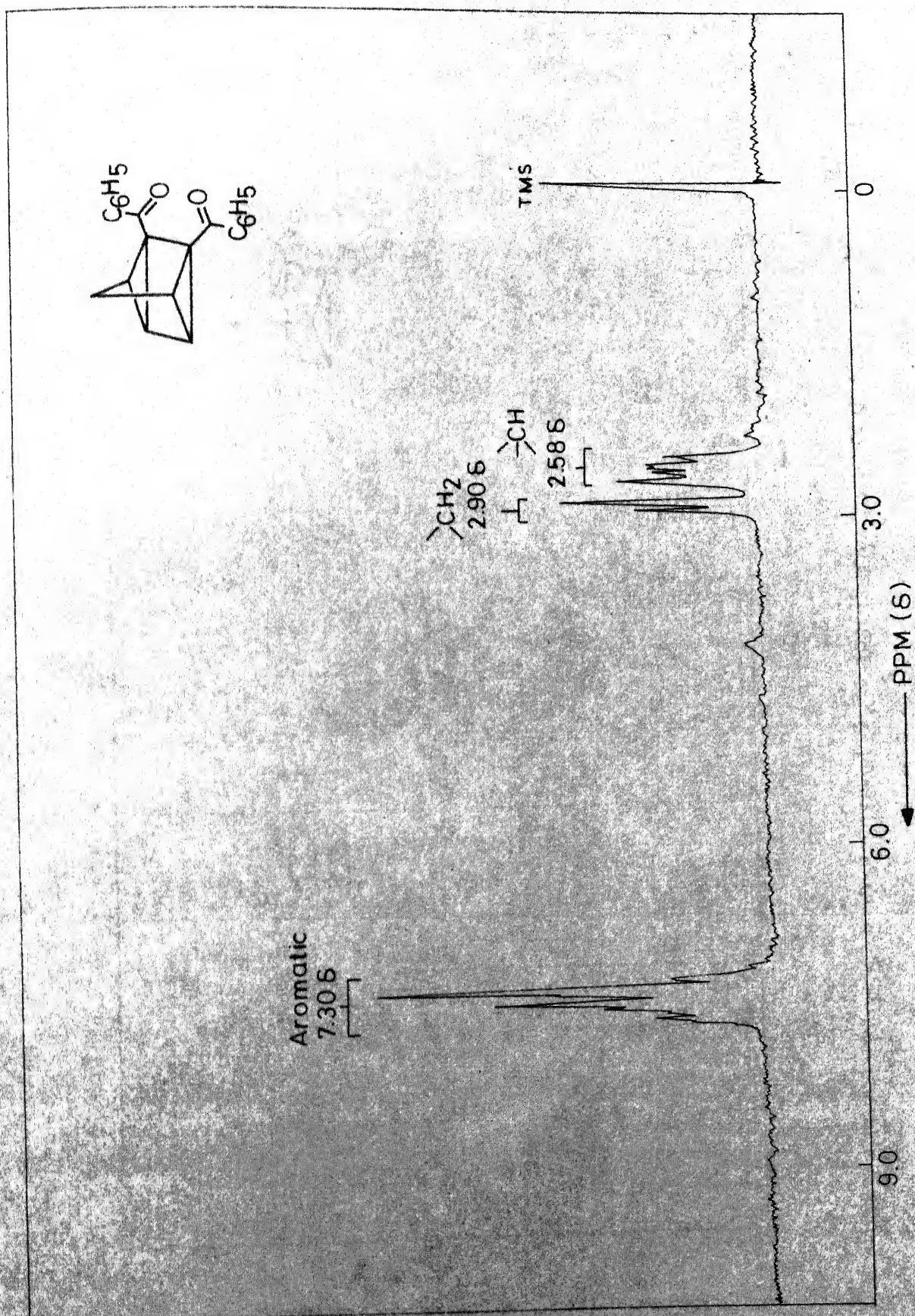


Fig. II.1 NMR spectrum(60MHz) of 2,3-dibenzoylquadracyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>] heptane (19)



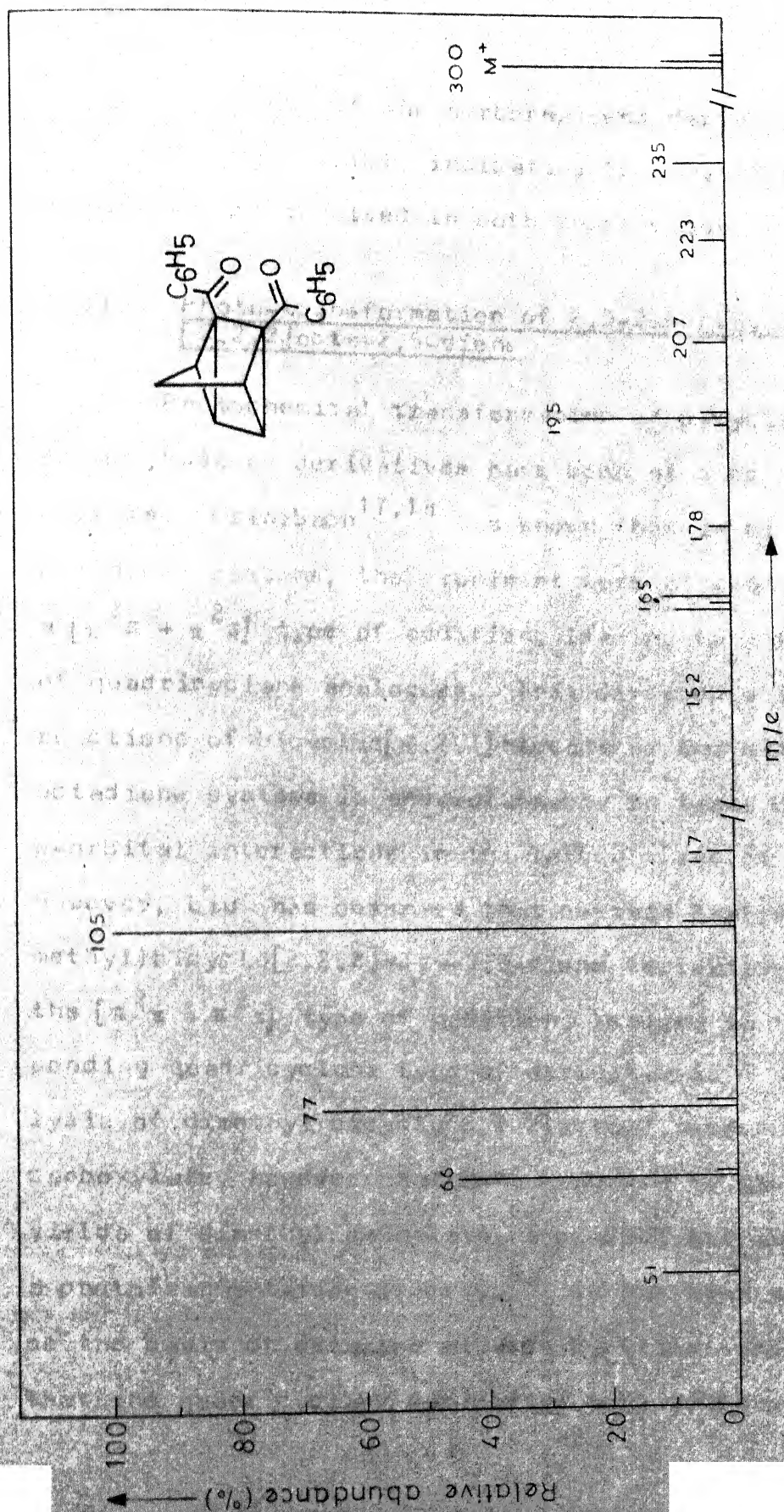


Fig. II.2 Mass spectrum of 2,3-dibenzoylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane(19)

similar to those of the norbornadiene derivative 18 (see, Chapter I, Fig. I.10), indicating thereby that common fragments are involved in both these cases.

### II.3.2 Photo-transformation of 2,3-Dibenzoylbicyclo- [2.2.2]octa-2,5-diene

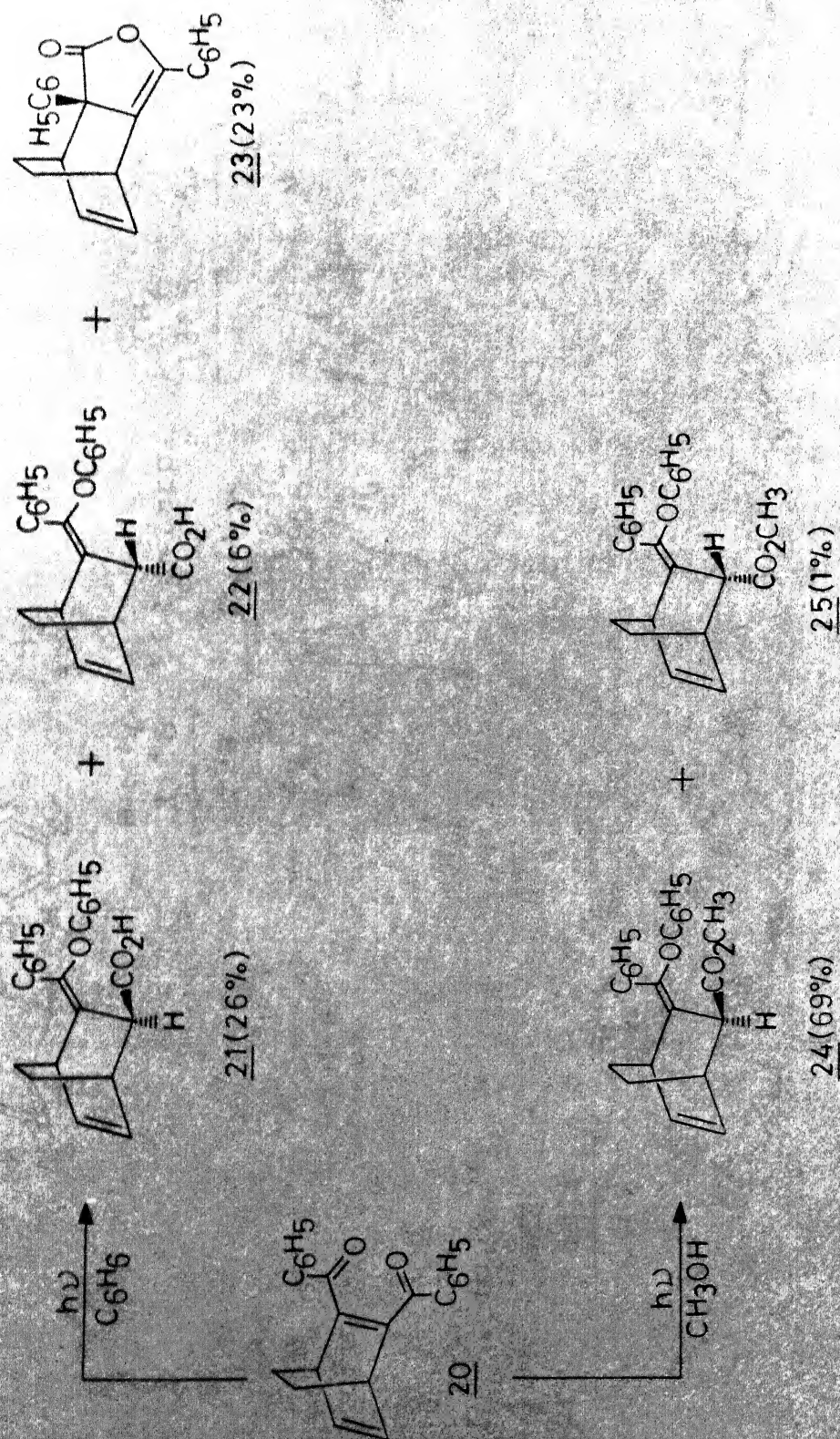
Photochemical transformation of bicyclo[2.2.2]-octa-2,5-diene derivatives have been studied by different workers. Prinzbach<sup>17,18</sup> has shown that in bicyclo[2.2.2]-octadiene systems, the prominent mode of reaction is not a  $[\pi^2s + \pi^2s]$  type of addition, leading to the formation of quadricyclane analogues. This difference in the photo-reactions of bicyclic[2.2.1]heptadiene and bicyclo[2.2.2]-octadiene systems is understandable in terms of the poorer p-orbital interactions in the latter class of compounds. However, Liu has observed that certain bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5-diene derivatives undergo the  $[\pi^2s + \pi^2s]$  type of addition, leading to the corresponding quadricyclane type of derivatives.<sup>19</sup> The photolysis of dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate, however, has been reported to give small yields of dimethyl phthalate, a product arising through a photofragmentation process.<sup>20</sup> It has been suggested, on the basis of detailed studies by Nelson and Gillespie,<sup>21</sup> that the quadricyclane derivative that is formed initially

in this reaction is undergoing a further reversion to the starting material, under the reaction conditions and hence the expected product has not been isolated.

In the present studies, we have examined the photochemical transformation of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (20). Photolysis of 20 in benzene solution for 3 1/2 hr, using a pyrex filter, resulted in the formation of a mixture of products consisting of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylic acid (21) (26%), 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-endo-carboxylic acid (22) (6%) and a lactone 23 (23%), isomeric with the starting material (Scheme II.8). The structures of these products have been established on the basis of elemental analysis and spectral data.

The nmr spectrum (Fig. II.3) of 21 showed two multiplets centred around  $1.53\delta$  (2H) and  $1.88\delta$  (2H), respectively, due to the methylene protons. The multiplets, centred around  $2.95\delta$  (1H) and  $3.58\delta$  (1H), respectively, have been assigned to the two bridgehead protons, whereas the doublet at  $3.28\delta$  (1H) has been assigned to the endo proton,  $H_2$ , ( $J_{1,2} = 2.5$  cps). Further splitting of this doublet due to a long-range coupling between  $H_2$  and  $H_7$ , protons ( $J_{2,7} = 1$  cps) confirmed the endo

Scheme II. 8





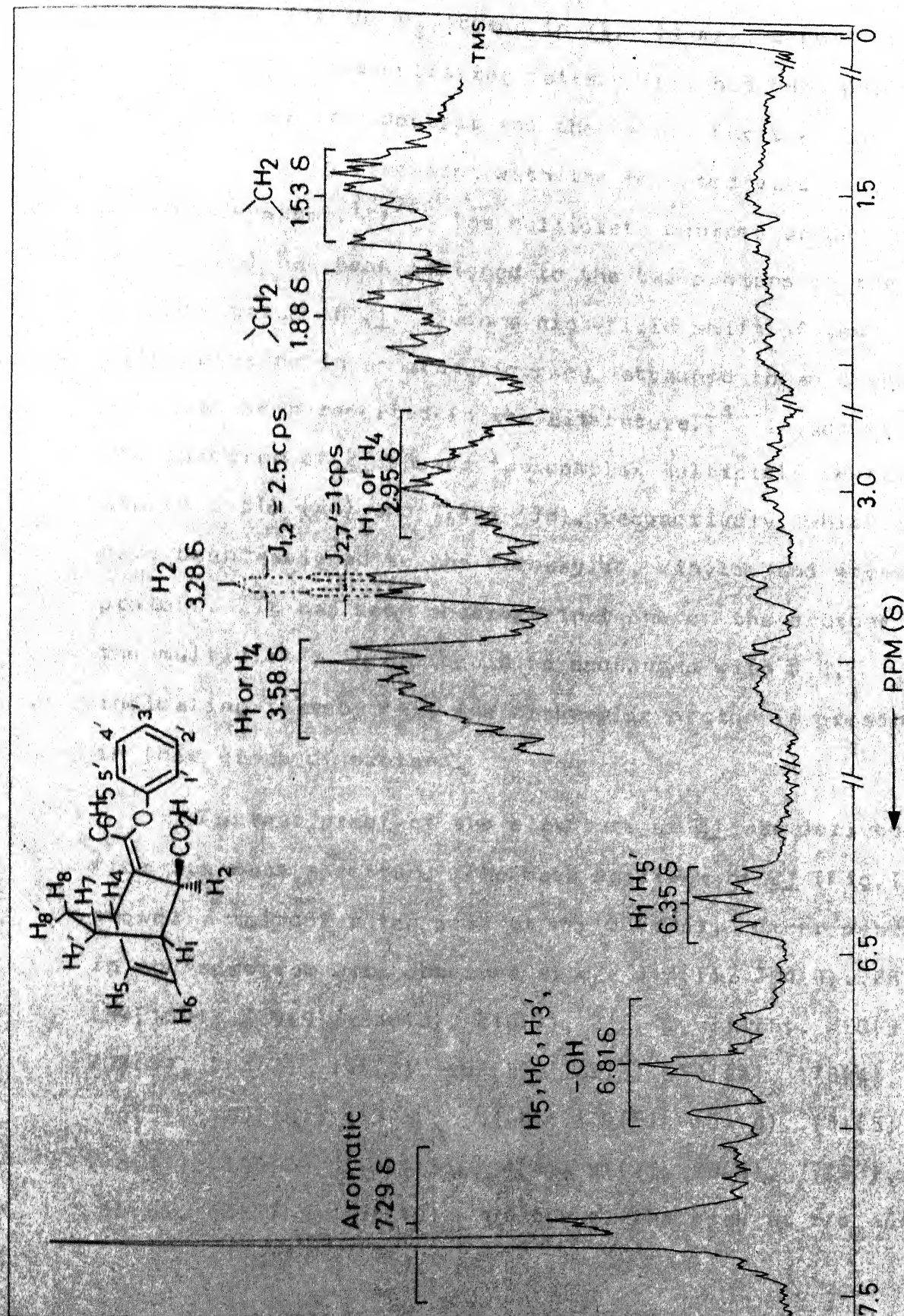


Fig. II. 3 NMR spectrum (60 MHz) of the exo-acid (21)

assignment for the  $H_2$ -proton in 21. It may be pointed out here that the splitting pattern that has been observed for the  $H_2$ -proton doublet and the values for the coupling constant are in agreement with the reported values for similar systems.<sup>22,23</sup> The multiplet, centred around  $6.35\delta$  (2H) has been assigned to the two protons of the phenoxy group in 21. Such a high-field shift of the ortho protons in an aromatic ring, attached to an oxygen atom has been reported in the literature.<sup>24</sup> In addition, the spectrum of 21 showed two complex multiplets centred around  $6.81\delta$  (4H) and  $7.29\delta$  (7H), respectively, which have been assigned to the carboxylic, vinylic and aromatic protons. It has been observed that one of the protons in the multiplet at  $6.81\delta$  could be exchanged with  $D_2O$ , indicating thereby that the carboxylic proton is present in this group of protons.

Further proof of the structure of 21 was derived from its mass spectrum. The mass spectrum of 21 (Fig.II.4) showed a molecular ion peak at  $m/e$  332(26). Other peaks in the spectrum were observed at  $m/e$  314(1), 304(4), 287(3), 259(100), 239(9), 238(6), 216(3), 215(2), 211(6), 210(9), 209(3), 194(2), 193(4), 183(8), 182(6), 181(3), 178(4), 166(5), 165(10), 153(5), 152(6), 139(2), 133(4), 131(5), 115(11), 105(22), 104(13), 94(4), 91(7), 78(6), 77(22), 65(5), 62(3) and 51(10). Of these, the peak at  $m/e$  304

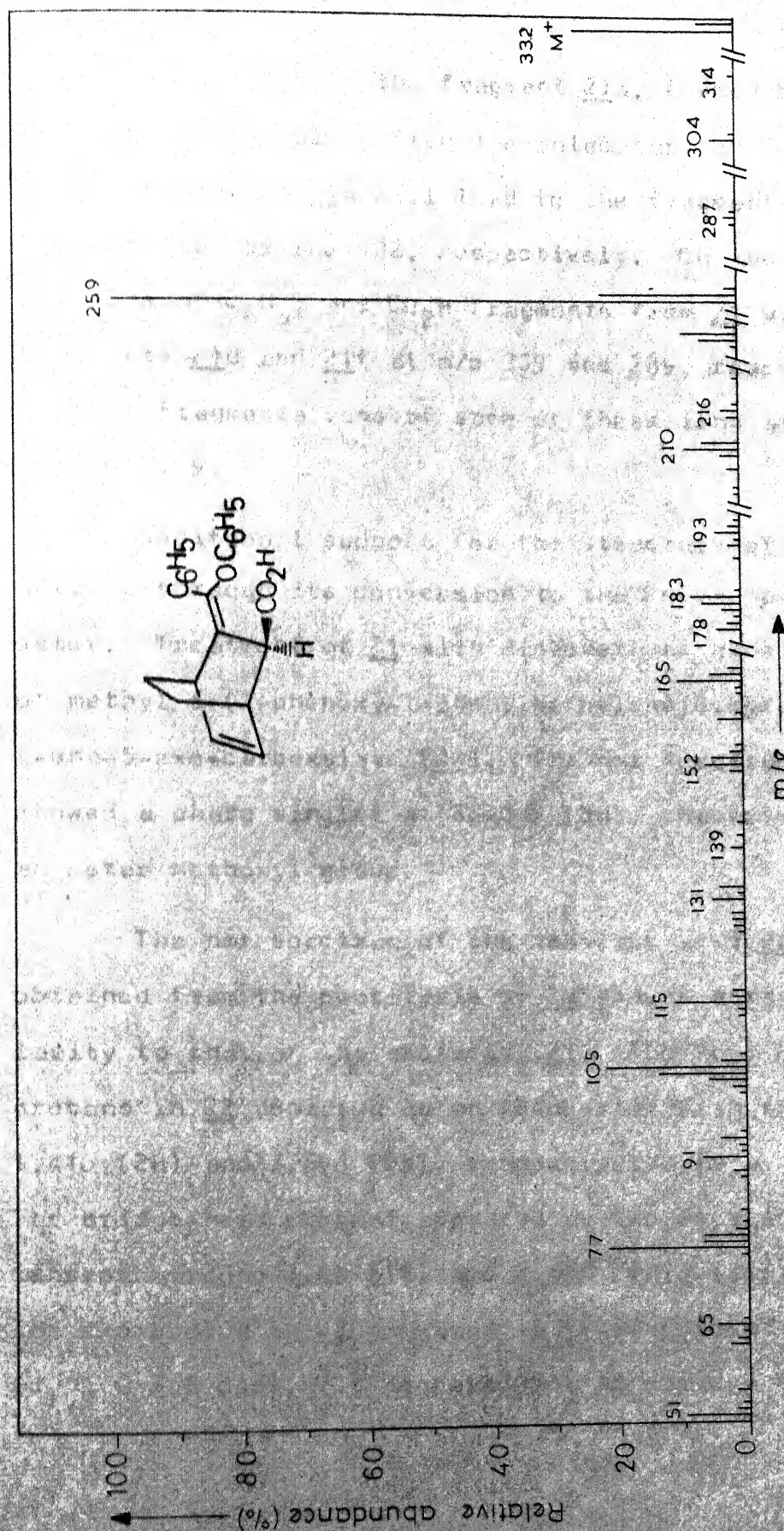


Fig.II.4 Mass spectrum of the exo-acid (21)

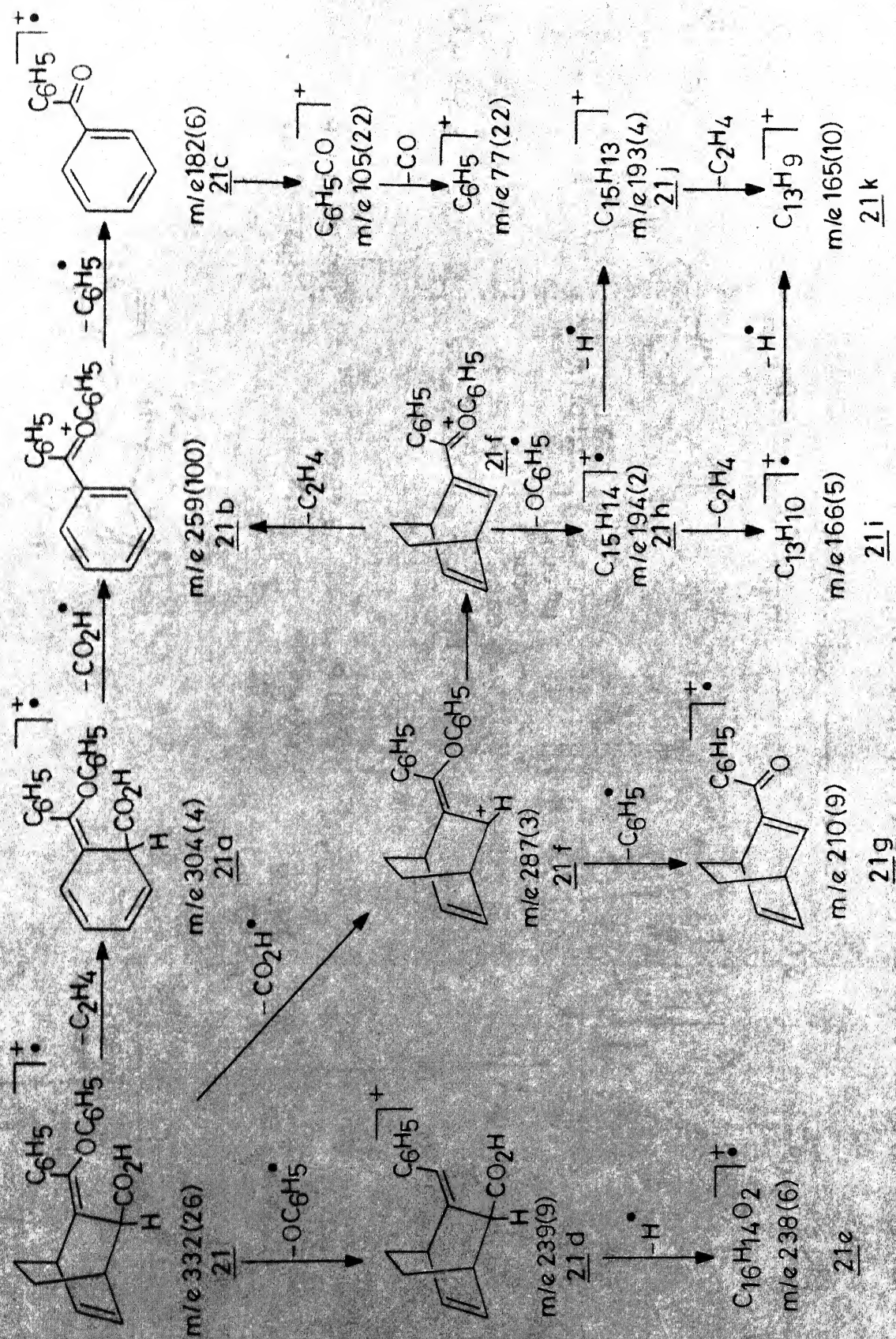
has been assigned to the fragment 21a, formed by the loss of an ethylene moiety from the molecular ion. Further fragmentation of 21a will lead to the fragments 21b and 21c at  $m/e$  259 and 182, respectively. On the other hand, the loss of  $C_6H_5O$  and  $CO_2H$  fragments from 21 will lead to fragments 21d and 21f at  $m/e$  239 and 289, respectively. Further fragmentations of some of these ions are shown in Scheme II.9.

Additional support for the structure of 21 was derived through its conversion to the corresponding methyl ester. Treatment of 21 with diazomethane gave a 57% yield of methyl 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylate (24). The nmr spectrum of 24 showed a sharp singlet at  $3.43\delta$  (3H), characteristic of an ester methoxyl group.

The nmr spectrum of the isomeric acid 22 (Fig. II.5), obtained from the photolysis of 20 showed striking similarity to that of the exo-acid, 21. The four methylene protons in 22 appeared as an AB-quartet with signals at  $1.41\delta$  (2H) and  $1.69\delta$  (2H), respectively, ( $J = 10$  cps). The bridge-head protons appeared as two sets of multiplets centred around  $3.0\delta$  (1H) and  $3.62\delta$  (1H), respectively. The exo-proton in 22 appeared as clean doublet at  $3.45\delta$  (1H) ( $J_{1,2} = 2.5$  cps). It is pertinent to observe that this



Scheme II.9



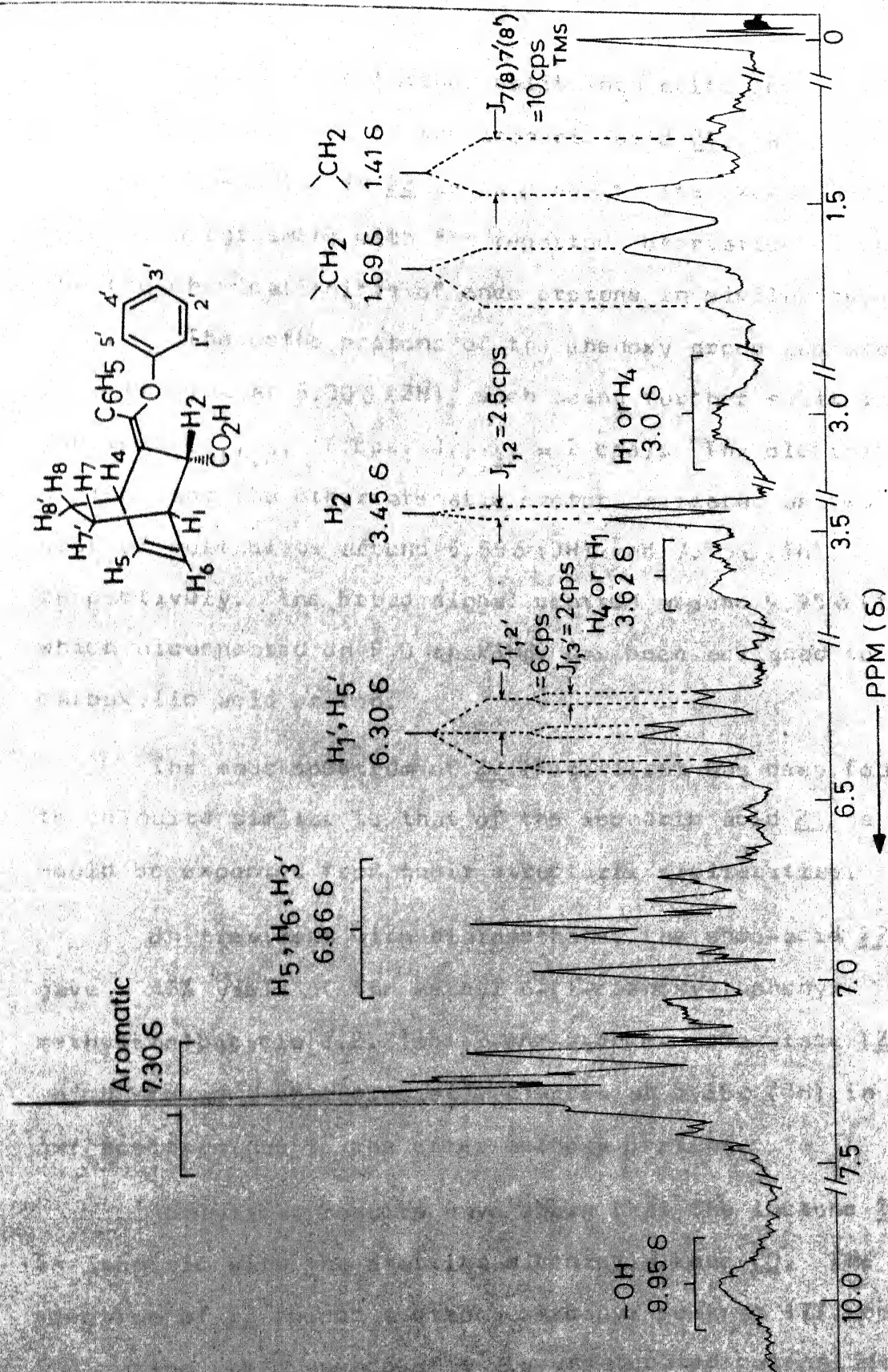


Fig.II.5 NMR spectrum(60MHz) of the endo-acid (22)

doublet has not been further split into multiplets, in contrast to the case of the isomeric acid 21. A down-field shift of H<sub>2</sub>-proton in 22 as compared to its exo-isomer, 21, is in agreement with the reported observation concerning the chemical shifts of endo protons in similar systems.<sup>25</sup> The ortho protons of the phenoxy group appeared as a triplet at 6.30  $\delta$  (2H), each being further split into doublets ( $J_{1,2}$ , 6 cps;  $J_{1,3}$ , = 2 cps). The olefinic protons and the other aromatic protons appeared as two sets of multiplets around 6.86  $\delta$  (3H) and 7.30  $\delta$  (7H), respectively. The broad signal centred around 9.95  $\delta$  (1H), which disappeared on D<sub>2</sub>O shaking, has been assigned to the carboxylic acid proton.

The mass spectrum of 22 (Fig. II.6) has been found to be quite similar to that of the isomeric acid 21, as would be expected from their structural similarities.

On treatment with diazomethane, the endo-acid, 22 gave a 43% yield of the methyl 6-(1-phenoxy-1-phenyl-methylene)bicyclo[2.2.2]oct-2-ene-5-endo-carboxylate (25), which showed a characteristic singlet at 3.38  $\delta$  (3H) in its nmr spectrum due to the ester methoxy protons.

Analytical results have shown that the lactone 23, is isomeric with the starting dibenzoylalkene 20. The ir spectrum of 23 showed a strong carbonyl peak at 1771 cm<sup>-1</sup>, indicating the presence of a  $\beta,\gamma$ -unsaturated butenolide.



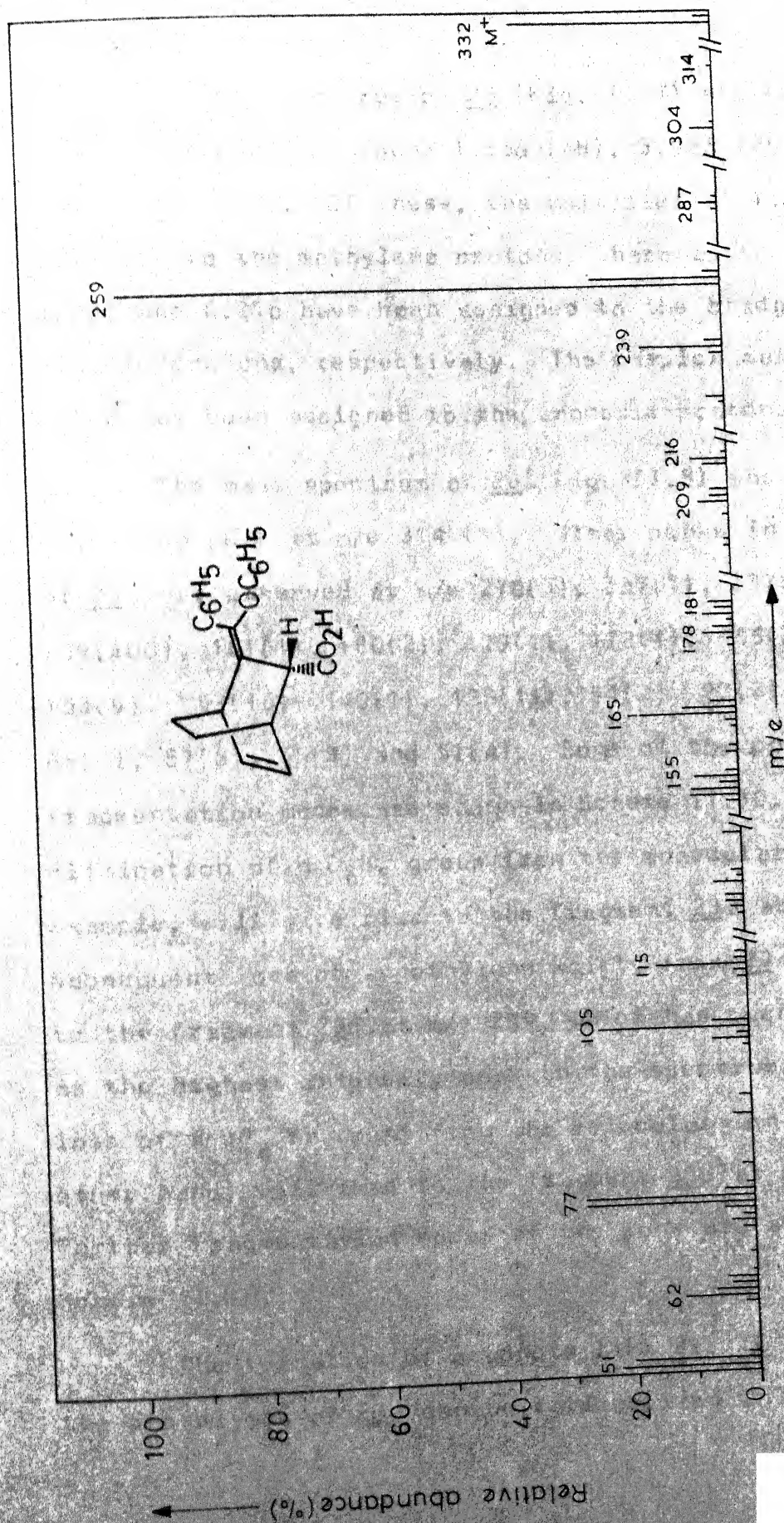


Fig.II.6 Mass spectrum of the endo-acid (22)

The nmr spectrum of 23 (Fig. II.7) showed several multiplets centred around 1.25 $\delta$  (4H), 3.98 $\delta$  (2H), 6.21 $\delta$  (2H) and 7.35 $\delta$  (10H). Of these, the multiplet at 1.25 $\delta$  has been assigned to the methylene protons, whereas, the ones at 3.98 $\delta$  and 6.21 $\delta$  have been assigned to the bridge-head and vinylic protons, respectively. The complex multiplet at 7.35 $\delta$  has been assigned to the aromatic protons.

The mass spectrum of 23 (Fig. II.8) showed a molecular ion peak at m/e 314 (1). Other peaks in the spectrum of 23 were observed at m/e 270(3), 257(1), 237(34), 209(100), 181(1), 180(2), 179(1), 178(1), 166(2), 165(4), 153(9), 152(16), 140(1), 105(11), 94(2), 93(2), 77(26), 65(8), 57(5), 55(3) and 51(4). Some of the possible fragmentation modes are shown in Scheme II.10. The facile elimination of a C<sub>6</sub>H<sub>5</sub> group from the molecular ion, for example, will give rise to the fragment 23a at m/e 237. Subsequent loss of an ethylene moiety from 23a will lead to the fragment 23c at m/e 209, which has been observed as the highest intensity peak in the spectrum. A direct loss of a CO<sub>2</sub> fragment from the molecular ion, on the other hand, will lead to the fragment 23b at m/e 270. Further fragmentation modes of the ions are shown in Scheme II.10.

The formation of products like 21, 22 and 23, in the photolysis of 20, can be rationalized in terms of the

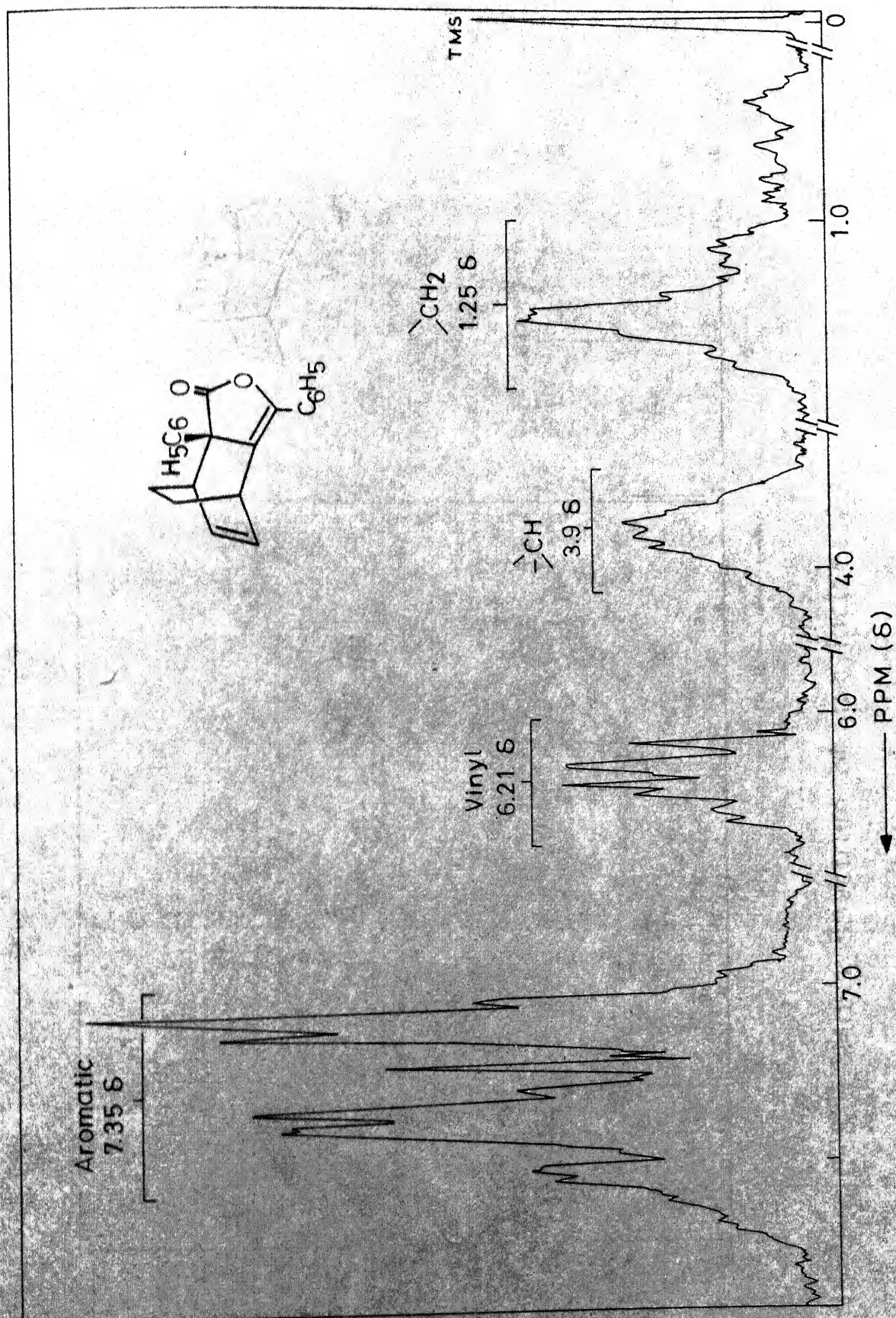


Fig. II. 7 NMR spectrum (60 MHz) of the lactone 23



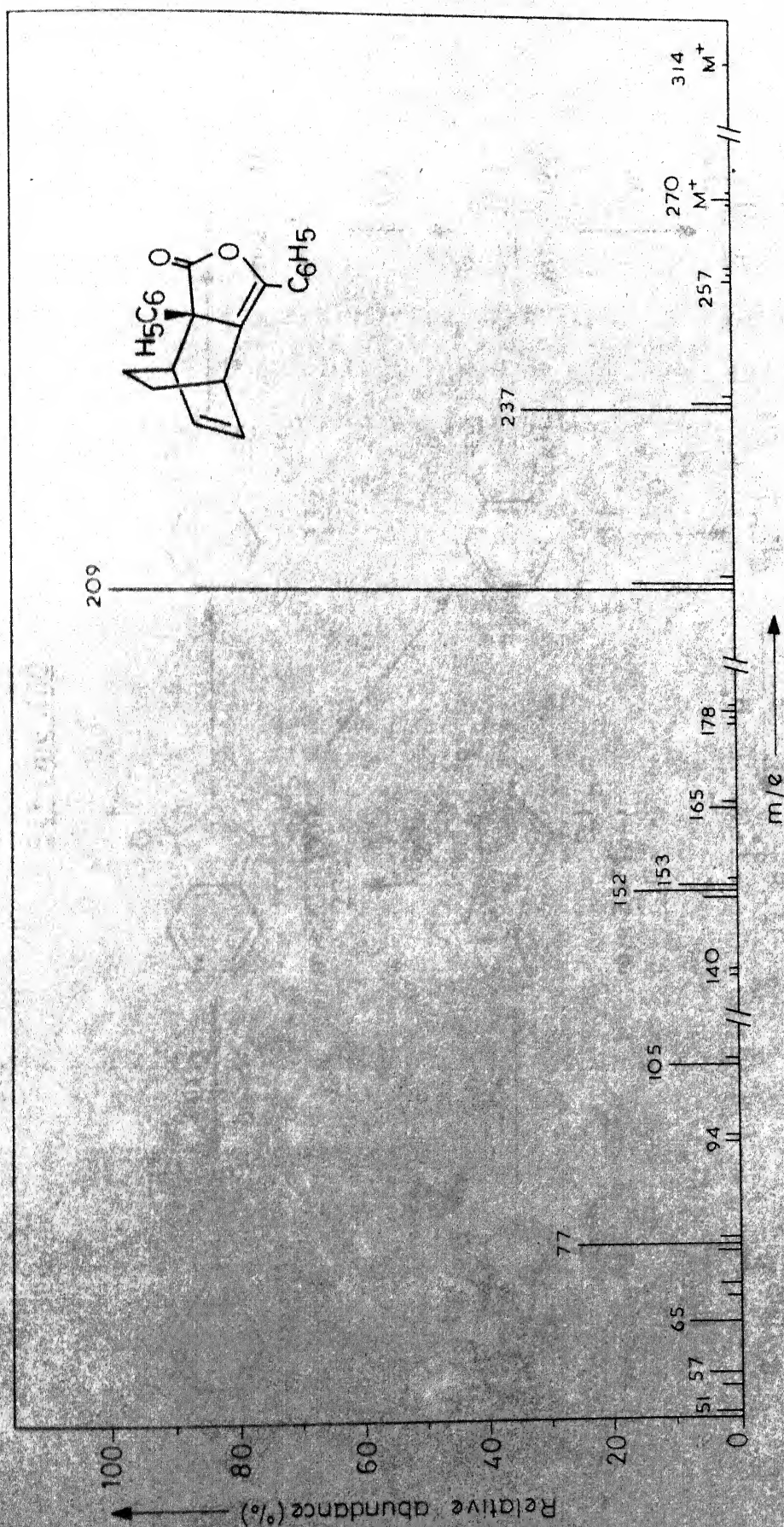
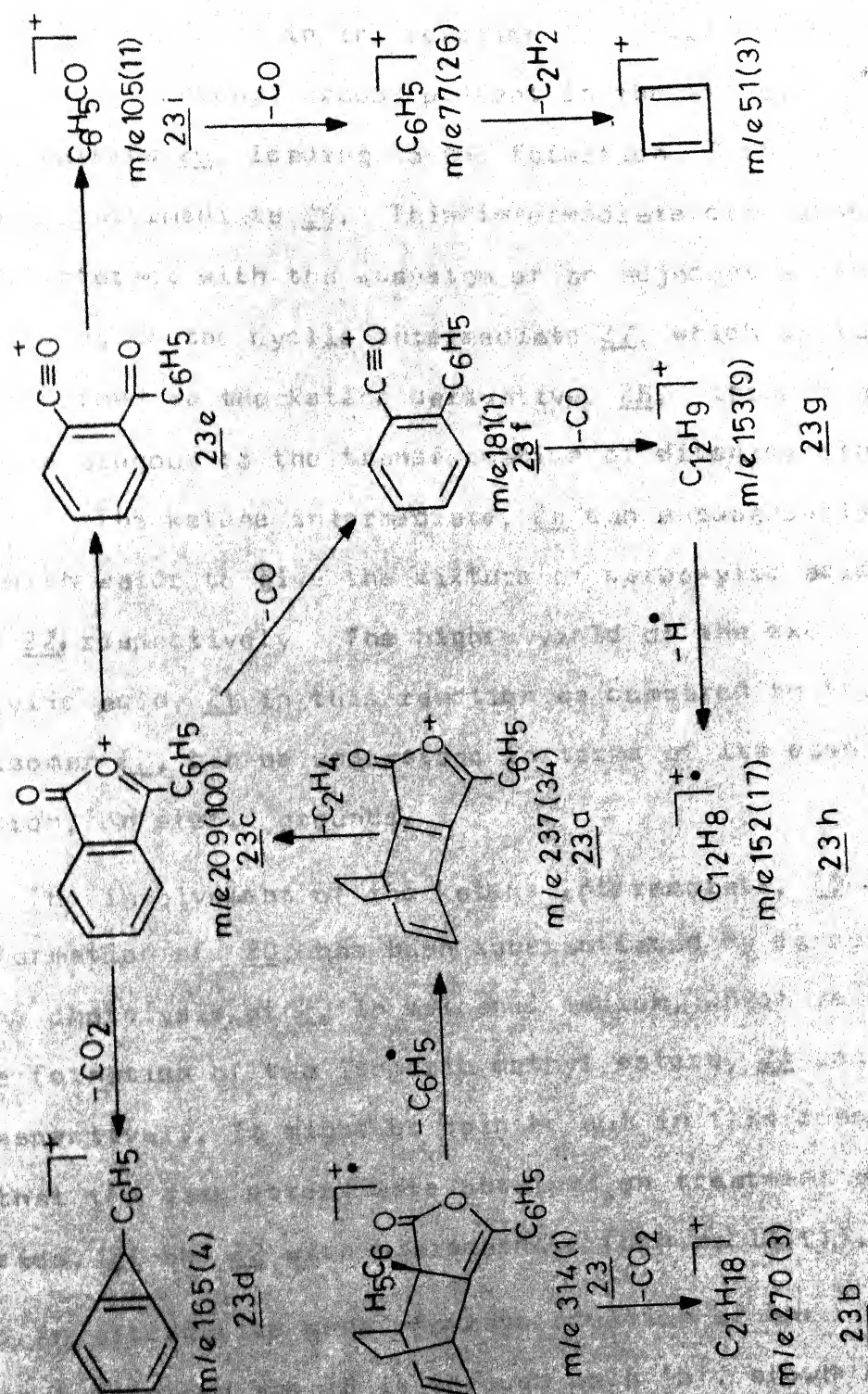


Fig. II. 8 Mass spectrum of the lactone 23

Scheme II.10



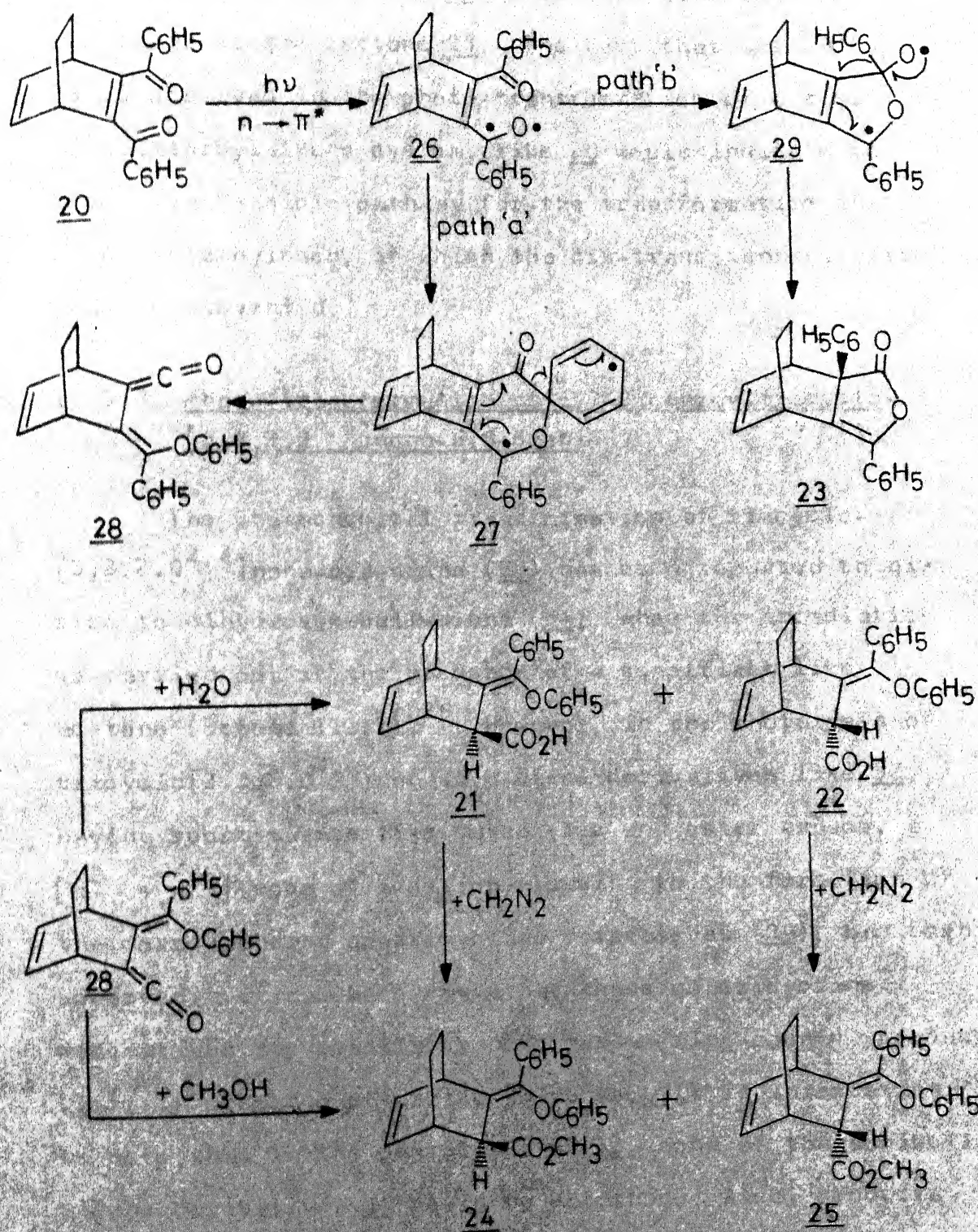


pathway shown in Scheme II.11. In this scheme, we assume that the initial step in the reaction is a  $n-\pi^*$  excitation of one of the carbonyl groups present in the starting dibenzoylalkene 20, leading to the formation of the diradical intermediate 26. This intermediate can subsequently interact with the  $\pi$ -system of an adjacent aromatic ring leading to the cyclic intermediate 27, which in turn is transformed to the ketene derivative, 28, through a pathway analogous to the transformation of dibenzoyl ethylenes.<sup>2-4</sup> The ketene intermediate, 28 can subsequently react with water to give the mixture of carboxylic acids, 21 and 22, respectively. The higher yield of the exo-carboxylic acid, 21 in this reaction as compared to the endo-isomer 22, can be understood in terms of its ease of formation, on steric grounds.

The involvement of the ketene intermediate, 28 in the transformation of 20, has been substantiated by carrying out the photolysis of 20 in methanol medium, which resulted in the formation of two isomeric methyl esters, 24 and 25, respectively. It might be pointed out in this connection that the same esters were obtained on treatment of the acids, 21 and 22 with diazomethane (Scheme II.11).

An alternative mode of transformation of the diradical intermediate 26 is through path 'b', shown in

Scheme II.11

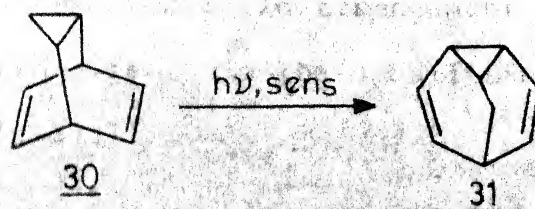


Scheme II.11. As per this scheme, the diradical 26 can interact with the  $\pi$ -system of the adjacent carbonyl group to give the intermediate 29, which can subsequently rearrange to the lactone 23. The fact that the lactone, 23 is observed in the photo-transformation of a rigid cis-dibenzoylalkene system, like 20 would indicate that this is a feasible pathway for the transformation of dibenzoylethylenes, in which the cis-trans isomerization mode is prevented.

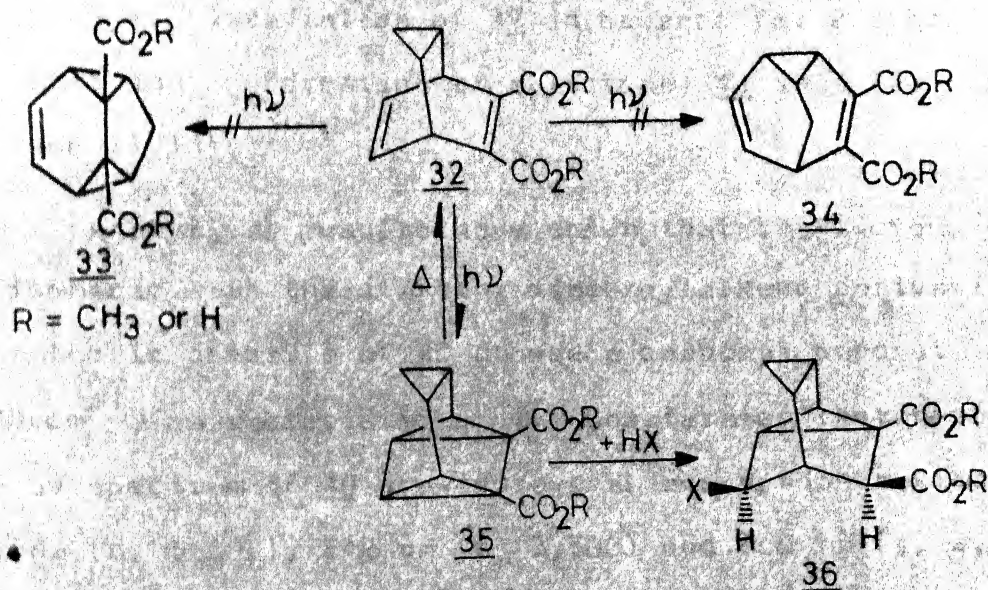
### II.3.3 Photo-transformation of 6,7-Dibenzoyltricyclo-[3.2.2.0<sup>2,4</sup>]nona-6,8-diene

The photochemical transformation of tricyclo-[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (30) has been reported to give rise to dihydrosemibullvalene (31), when the irradiation is carried out in the presence of a sensitizer like acetone (Scheme II.12).<sup>26</sup> However, in the photolysis of tricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene derivatives like 32, having substituents like carboxylic and ester groups, a  $[\pi^2s + \pi^2s]$  mode of addition, leading to the formation of the corresponding quadricyclane derivatives (35), has been observed. It has been shown that these quadricyclane derivatives are readily transformed to ring-opened products (36), in presence of protic solvents. It is interesting to note that in the photolysis of 32, none of the semibullvalene derivative, 34 could be obtained. Also, products

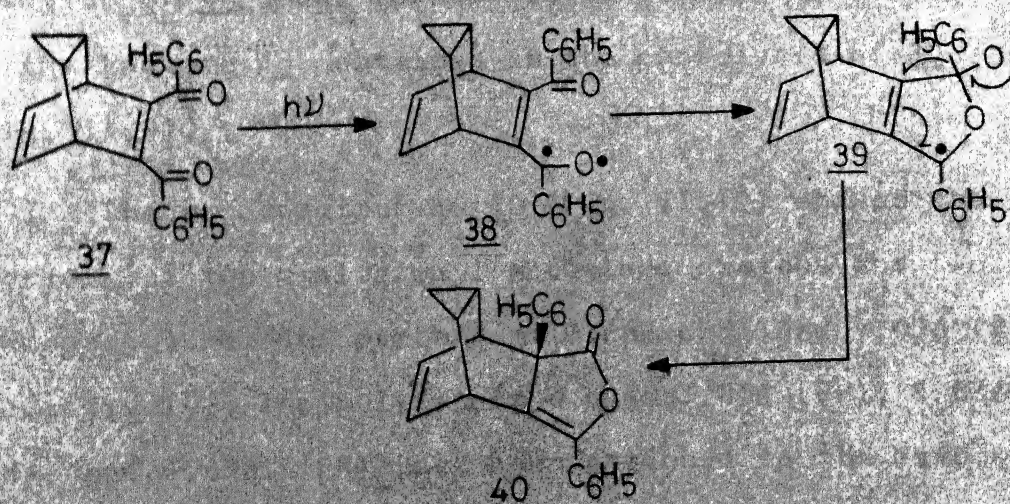
Scheme II.12



Scheme II.13



Scheme II.14





like 33, resulting from a  $[\pi^2_s + \pi^2_s]$  type of addition of 32, have not been observed, inspite of the stereochemically favourable exo-arrangement of the three-membered ring vis-a-vis the substituted double bond (Scheme II.13).<sup>27</sup>

In the present investigation, we have examined the photolysis of 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (37). Irradiation of 37 in benzene for 2½ hr resulted in the formation of a lactone, 40 in a 33% yield (Scheme II.14).

Analytical results have shown that the lactone 40 is isomeric with the starting dibenzoylalkene derivative, 37. The ir spectrum of 40 showed a carbonyl band at 1770  $\text{cm}^{-1}$ , characteristic of  $\beta,\gamma$ -unsaturated lactones. The uv spectrum of 40 showed several absorption maxima at 230 nm ( $\epsilon$ , 5,000), 242 nm ( $\epsilon$ , 3,500) and 260 nm ( $\epsilon$ , 2,500). It might be pointed out in this connection that the uv spectrum of 40 shows remarkable similarity to the spectrum of the lactone 23, obtained in the photolysis of 20 (Fig. II.9).

The nmr spectrum of 40 (Fig. II.10) showed the presence of two cyclopropyl methylene protons and two cyclopropyl methine protons at 0.66 $\delta$  (2H) and 1.40 $\delta$  (2H), respectively. The multiplets around 3.85 $\delta$  (2H), 5.82 $\delta$  (2H), and 7.25 $\delta$  (10H) have been assigned to the bridge-head, vinylic and aromatic protons, respectively.

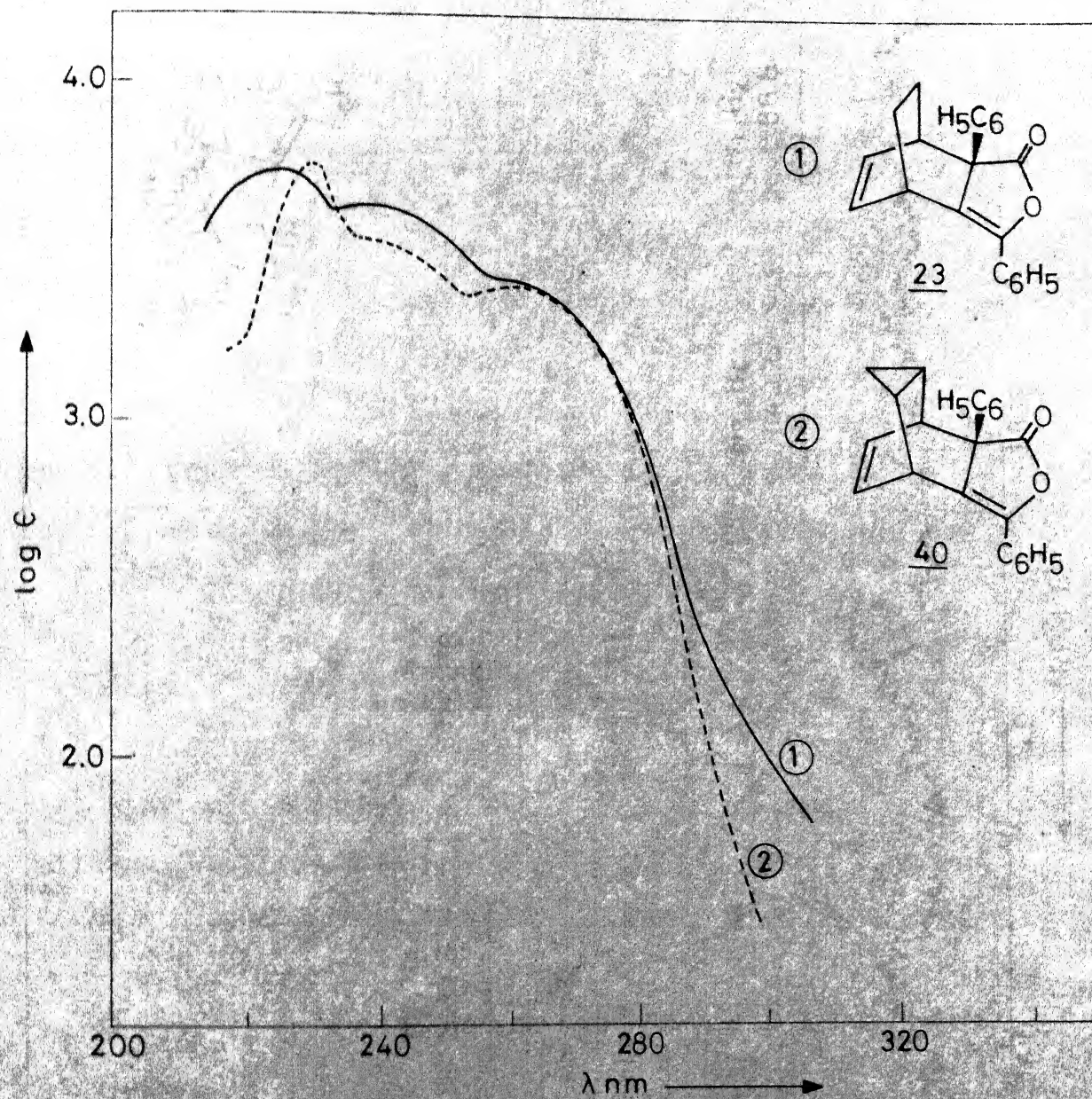


Fig.II.9 UV spectra of 23 and 40

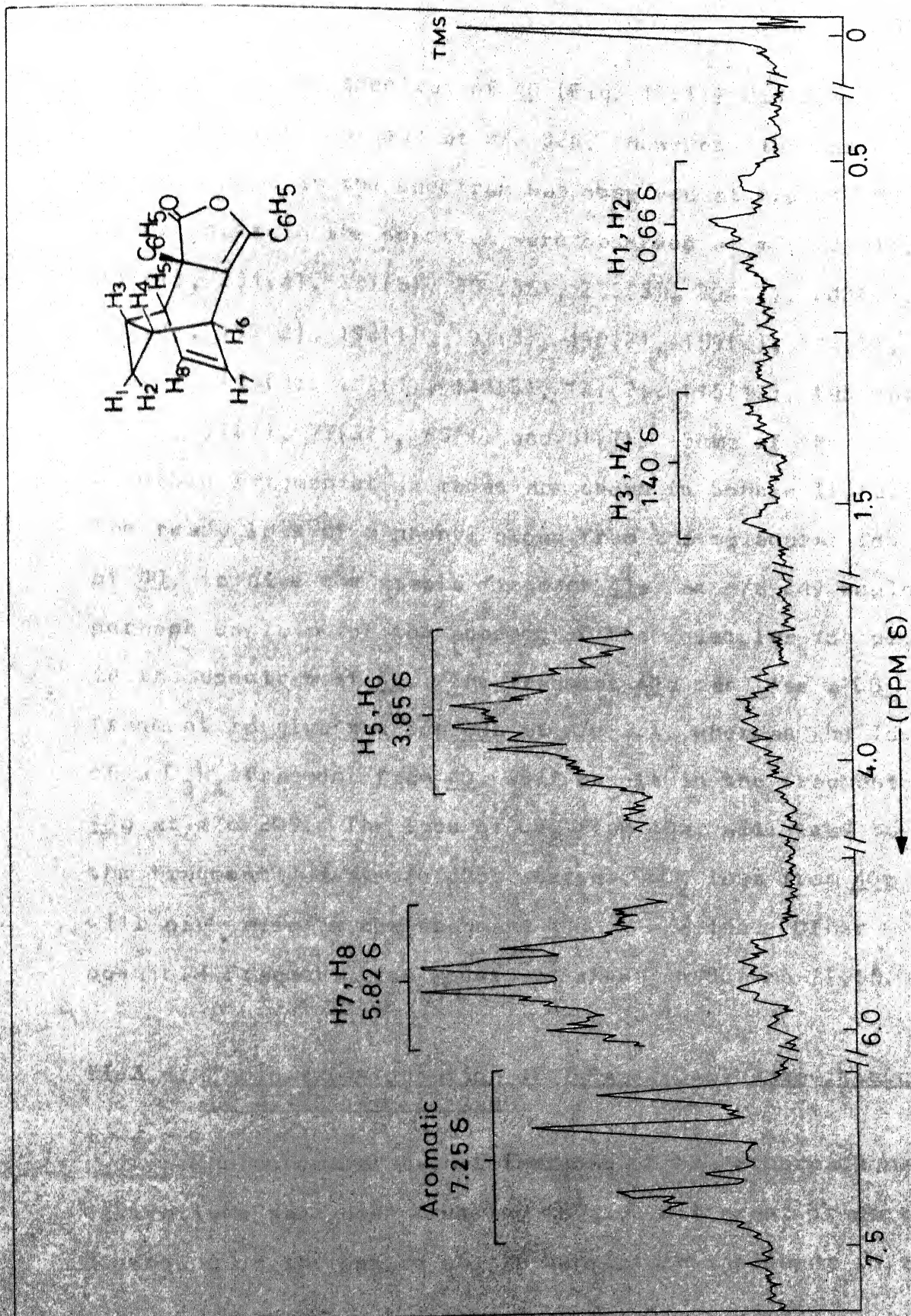


Fig. II. 10 NMR spectrum (60MHz) of the lactone 40

The mass spectrum of 40 (Fig. II.11) did not show the molecular ion peak at  $m/e$  326. However, the most intense peak in the spectrum was observed at  $m/e$  249(100). Other peaks in the spectrum were observed at  $m/e$  234(1), 232(1), 231(4), 221(5), 209(35), 205(3), 204(2), 203(5), 202(3), 193(2), 192(1), 191(3), 190(2), 189(2), 178(5), 165(6), 153(3), 152(7), 143(3), 127(2), 115(13), 105(76), 94(5), 91(7), 77(37), 65(9) and 51(7). Some of the probable fragmentation modes are shown in Scheme II.15. The ready loss of a phenyl group from the molecular ion of 40, to give the stable fragment 40a, at  $m/e$  249 would perhaps explain for the absence of the molecular ion peak in the spectrum of 40. The fragment 40a can lose a CO fragment to give the ion 40b at  $m/e$  221, whereas the loss of a  $C_3H_4$  fragment from 40a will result in the fragment 40g at  $m/e$  209. The loss of  $CO_2$  from 40a, will lead to the fragment 40i at  $m/e$  205, whereas,  $CO_2$  loss from 40g will give rise to the fragment 40h at  $m/e$  165. Other possible fragmentation modes are shown in Scheme II.15.

#### II.3.4 Photo-transformation of 7-Oxe-2,3-dibenzoylbicyclo-[2.2.1]hepta-2,5-diene

Photochemical transformations of oxanorbornadiene derivatives have been reported to give different products, depending on the nature of the substituents present in the



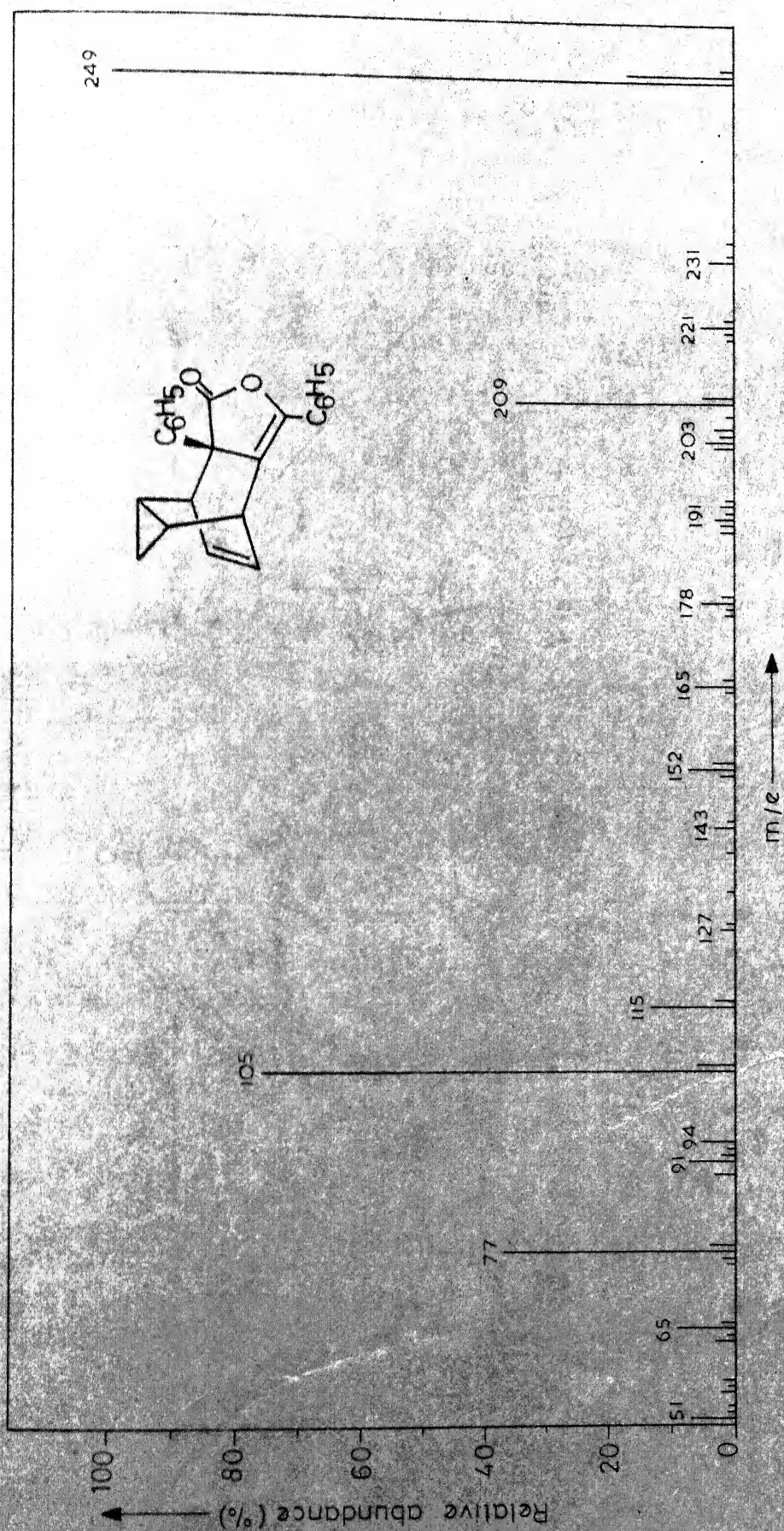


Fig. II.11 Mass spectrum of the lactone 40

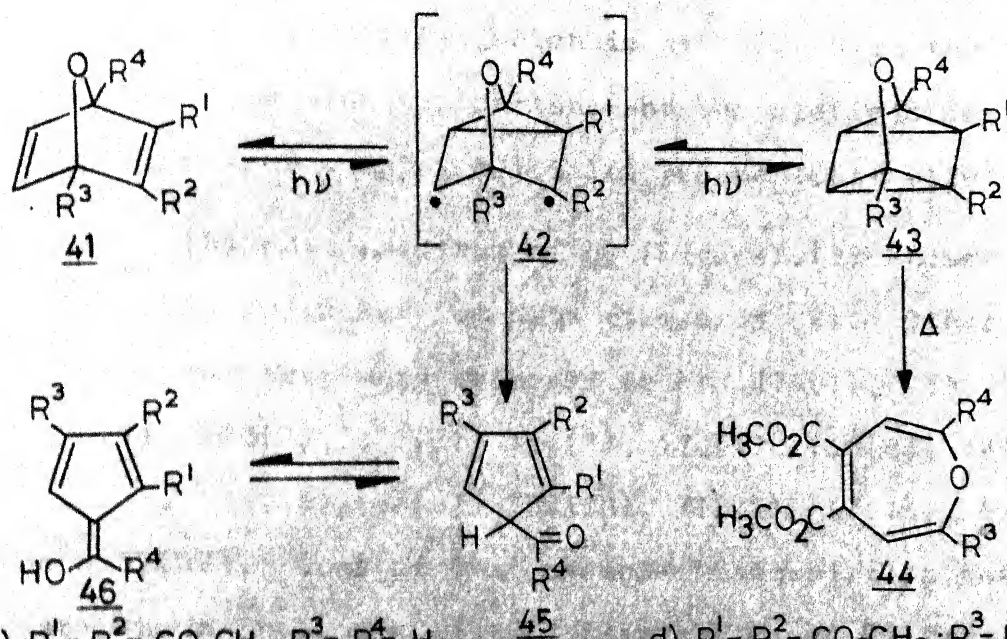


starting material. Thus, it has been observed that the photolysis of the oxanorbornadienes, 41a-f, for example, lead to the corresponding oxaquadricyclanes, 43a-f.<sup>28</sup> Prinzbach and coworkers<sup>29-33</sup> have observed that the oxaquadricyclanes, 43d-f undergo further transformation to give the corresponding oxepine derivatives, 44d-f. A second possible pathway for the photo-transformation of oxa-norbornadienes is through a di- $\pi$ -methane rearrangement, leading to the formation of fulvene derivatives. Thus, it has been observed that the photolysis of the oxa-norbornadienes, 41a-c, give rise to the corresponding 6-hydroxyfulvenes, 46a-c (Scheme II.16). It is known that oxa-quadricyclanes are isomerized to the corresponding hydroxyfulvenes under Ag or Cu-ion catalysis.<sup>34</sup> Quite recently, Bansal et al.<sup>35</sup> have reported similar isomerization of oxa-quadricyclanes to oxepine derivatives and hydroxyfulvenes through iodine-catalyzed reactions.

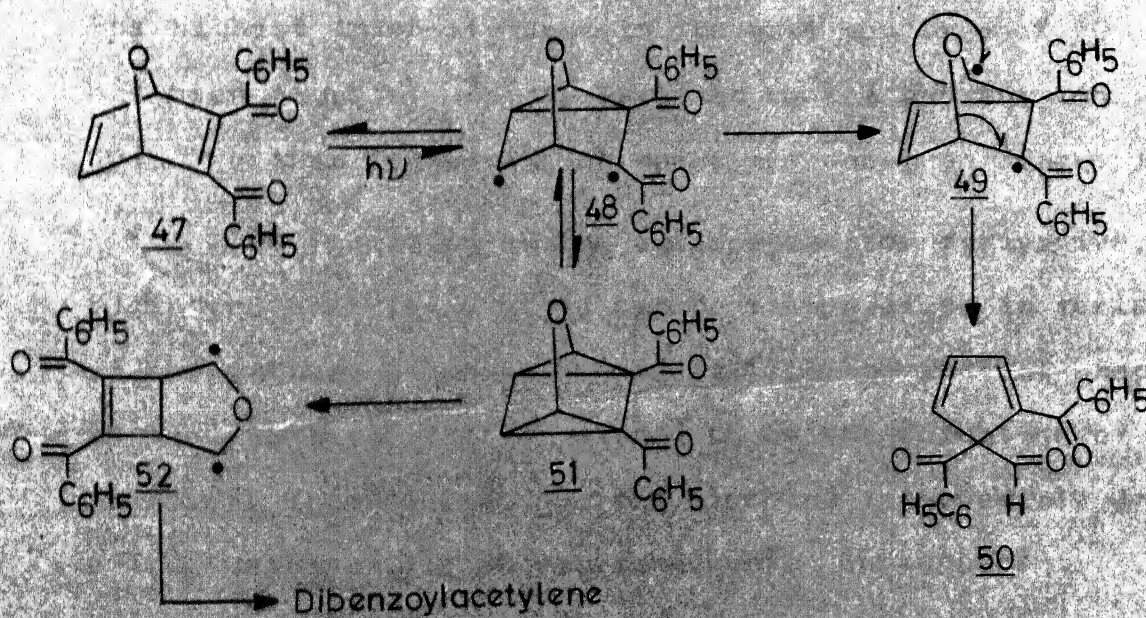
In the present investigation, we have examined the photochemical transformation of an oxa-norbornadiene system, like 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (47). Irradiation of 47 in benzene, using a 2539 Å light source, for 2½ hr gave a mixture of products consisting of dibenzoylacetylene (13%) and a product, tentatively identified as 1,5-dibenzoyl-5-formyl-1,3-cyclopentadiene (50) (32%) (Scheme II.17).



Scheme II.16

a)  $R^1 = R^2 = \text{CO}_2\text{CH}_3$ ;  $R^3 = R^4 = \text{H}$ b)  $R^1 = R^2 = \text{CO}_2\text{CH}_3$ ;  $R^3 = R^4 = \text{CH}$ c)  $R^1 = R^2 = \text{CO}_2\text{CH}_3$ ;  $R^3 = \text{H}$ ;  $R^4 = \text{CH}(\text{OC}_2\text{H}_5)_2$ d)  $R^1 = R^2 = \text{CO}_2\text{CH}_3$ ;  $R^3 = \text{H}$ ;  $R^4 = \text{C}_6\text{H}_5$ e)  $R^1 = R^2 = \text{CO}_2\text{CH}_3$ ;  $R^3 = R^4 = \text{C}_6\text{H}_5$ f)  $R^1 = R^2 = R^3 = R^4 = \text{H}$ 

Scheme II.17



The nmr spectrum of 50 (Fig. II.12) showed a sharp singlet at  $9.75\delta$  (1H), which is attributed to the formyl proton. The aromatic protons and the olefinic protons appeared as a complex multiplet around  $7.63\delta$  (13H).

The mass spectrum of 50 (Fig. II.13) showed a low-intensity molecular ion peak at  $m/e$  302(8). Other peaks in the spectrum were observed at  $m/e$  274(1), 273(1), 255(1), 225(2), 223(2), 197(3), 178(1), 169(2), 147(2), 139(3), 105(16), 83(8), 78(100), 77(32), 62(16), 52(25) and 51(32). Some of the possible fragmentation modes are shown in Scheme II.18. Elimination of CO from the molecular ion, for example, will lead to the fragment 50a at  $m/e$  274, which in turn can lose a  $C_6H_5$  group to give the fragment 50b at  $m/e$  197. Further loss of CO from 50b will result in the fragment 50c, at  $m/e$  169. The highest intensity peak in the mass spectrum of 50 has been found at  $m/e$  78, assigned to the benzene ion 50d. Further fragmentation modes are shown in Scheme II.18.

The formation of the cyclopentadiene derivative, 50 in the photolysis of 47 can be rationalized in terms of the pathway shown in Scheme II.17. The initial step in the photoreaction is assumed to be the formation of a diradical intermediate 48, the expected intermediate in a di- $\pi$ -methane type of rearrangement. Subsequent

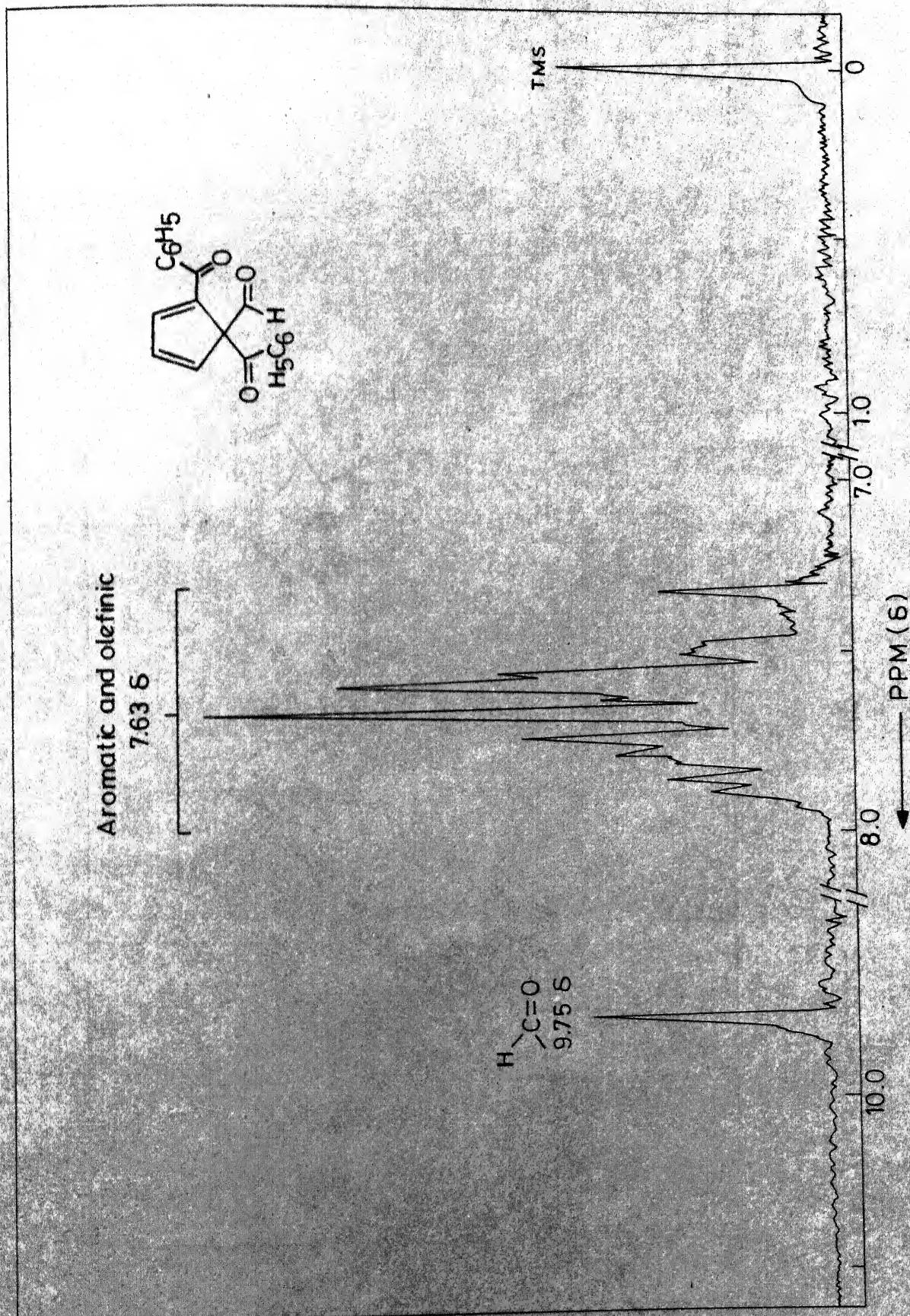


Fig. II.12 NMR spectrum (60 MHz) of 1,5-dibenzoyl-5-formyl-1,3-cyclopentadiene (50)



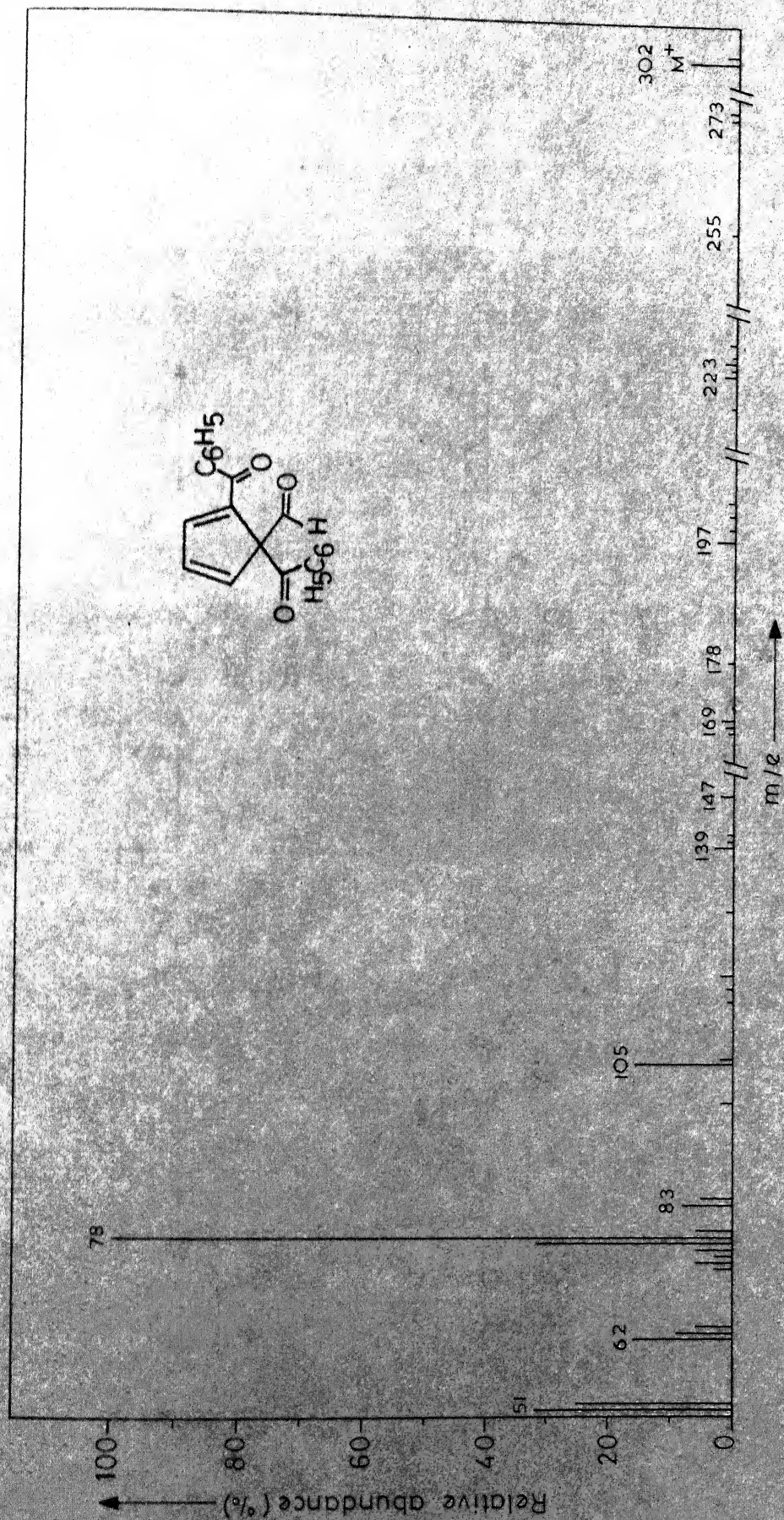
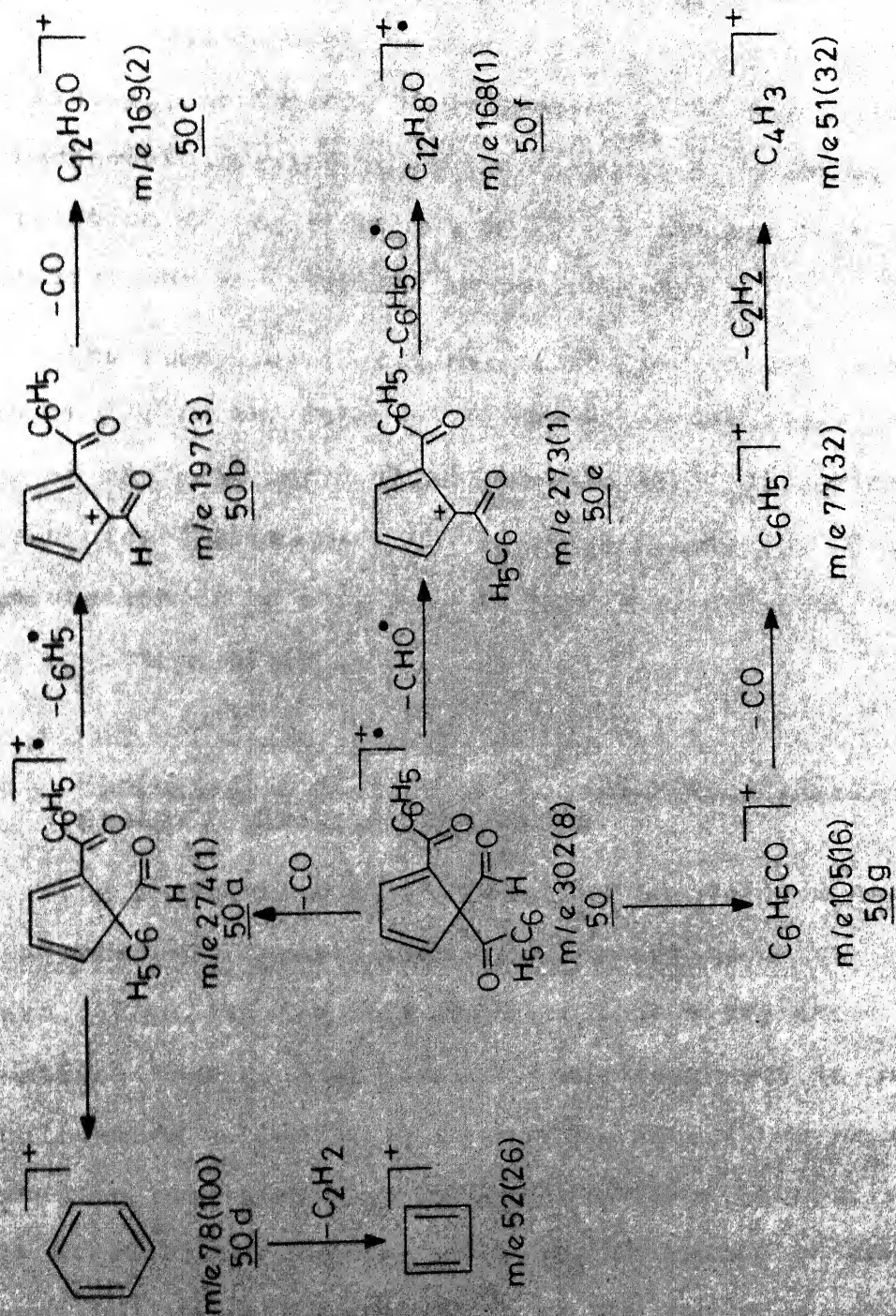


Fig. II.13 Mass spectrum of 1,5-dibenzoyl-3-cyclopentadiene (50)

Scheme II.18





transformation of 48 would lead to the formation of 50, through a second diradical intermediate, 49. Mention may be made in this connection that a cyclopentadiene derivative like 50, is capable of undergoing [1,5]-sigmatropic rearrangements leading to isomeric products. Further confirmation of the structure of 50 and its possible isomerizations are still to be investigated.

The formation of dibenzoylacetylene in the photolysis of 47, on the other hand, may be rationalized in terms of the oxaquadricyclane intermediate (51), which can subsequently fragment to the intermediate 52. Further fragmentation of 52 will lead to dibenzoylacetylene as shown in Scheme II.17.

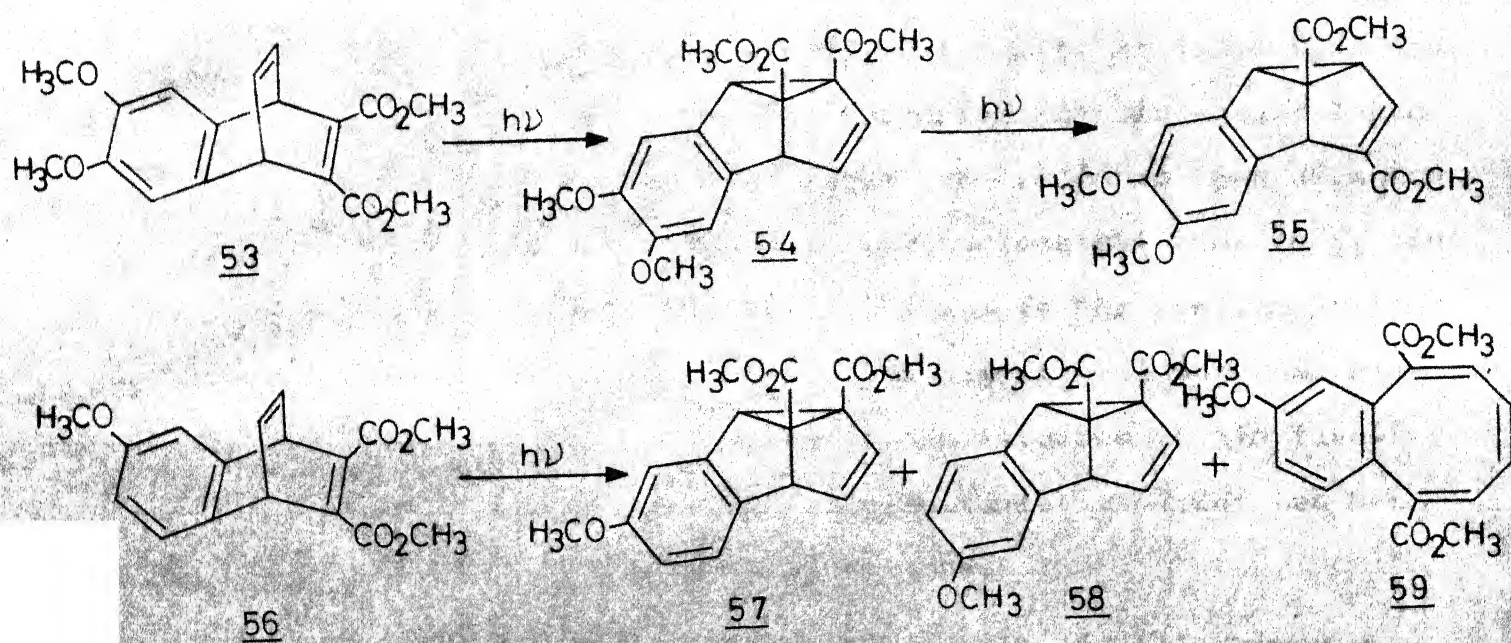
#### II.3.5 Photo-transformation of 9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene

The photochemistry of barrelene derivatives has been extensively investigated by different group of workers. Thus, it has been observed that barrelene derivatives undergo a di- $\pi$ -methane rearrangement to give semibullvalene derivatives.<sup>36</sup> Benzobarrelene has been reported to give rise to a cyclooctatetraene derivative, on direct irradiation, whereas under the influence of sensitizers, benzosemibullvalene is formed.<sup>37</sup> On the basis of detailed investigations of deuterated benzobarrelene derivatives,

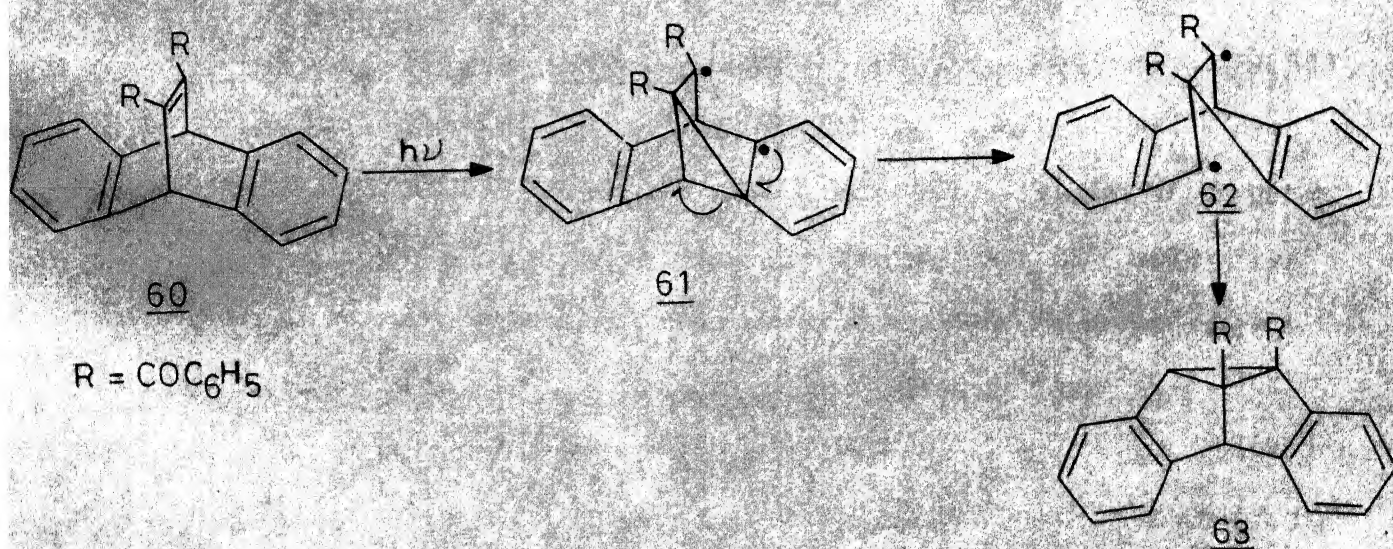
it has been shown that the di- $\pi$ -methane rearrangement in these systems takes place through a vinyl-vinyl bridging process and not through benzo-vinyl bridging. The photochemistry of several substituted dibenzobarrelene systems has been studied by Ciganek who has shown that in all these cases, dibenzosemibullvalenes are formed.<sup>38</sup> Recently, Bender and coworkers<sup>39</sup> have examined the effect of polar **substituent**, in the di- $\pi$ -methane rearrangement of some benzobarrelene derivatives like 53 and 56 (Scheme II.19). They have observed that the photo-transformation of 53, for example, leads to the formation of the benzosemibullvalene, 54, which in turn undergoes a further photo-rearrangement to give the isomeric benzosemibullvalene, 55. The direct photolysis of 56, on the other hand, gave rise to a mixture of products consisting of two isomeric benzosemibullvalenes, 57 and 58, and a benzocyclooctatetraene derivative, 59. In presence of a sensitizer, only 57 and 58 were formed in the photolysis of 56 (Scheme II.19).

In our present studies, we have examined the photochemical transformation of a dibenzoyl substituted dibenzobarrelene derivative like 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (60). Photolysis of 60 in benzene solution for 4 hr gave a 88% yield of a product, identified as 1,2-dibenzoyldibenzotricyclo[3.3.0.0<sup>2,8</sup>]octadiene (63)

Scheme II.19



Scheme II.20



(Scheme II.20). The structure of 63 was determined on the basis of analytical results and spectral data. Analytical data showed that the product 63 is isomeric with the starting material 60. The nmr spectrum of 63 (Fig. II.14) showed two sharp singlets at 4.24 $\delta$  (1H) and 4.64 $\delta$  (1H) and a complex multiplet centred around 7.26 $\delta$  (18H). Of these, the singlet at 4.24 $\delta$  has been assigned to the tertiary proton of the cyclopropyl ring in 63, in analogy to the chemical shift values for similar protons in related systems.<sup>38-40</sup> The signal at 4.64 $\delta$  has been assigned to the tertiary proton attached to the five-membered ring systems. The multiplet at 7.26 $\delta$  has been assigned to the aromatic protons.

The mass spectrum of 63 (Fig. II.15) showed a molecular ion peak at m/e 412 (62). Other peaks in the spectrum were observed at m/e 307(55), 279(60), 278(30), 277(13), 272(12), 229(16), 202(36), 201(10), 200(13), 177(3), 176(2), 175(1), 152(2), 146(3), 105(100), 78(55), 77(45), 76(15), 75(4), 74(9), 52(29) and 51(30). Some of the possible fragmentation modes are shown in Scheme II.21. The loss of a benzoyl group from the molecular ion, for example, will give rise to the fragment 63a at m/e 307. Further loss of a CO group from 63a will lead to the fragment 63b at m/e 279, whereas the loss of a phenyl group from 63a will lead to the fragment 63d



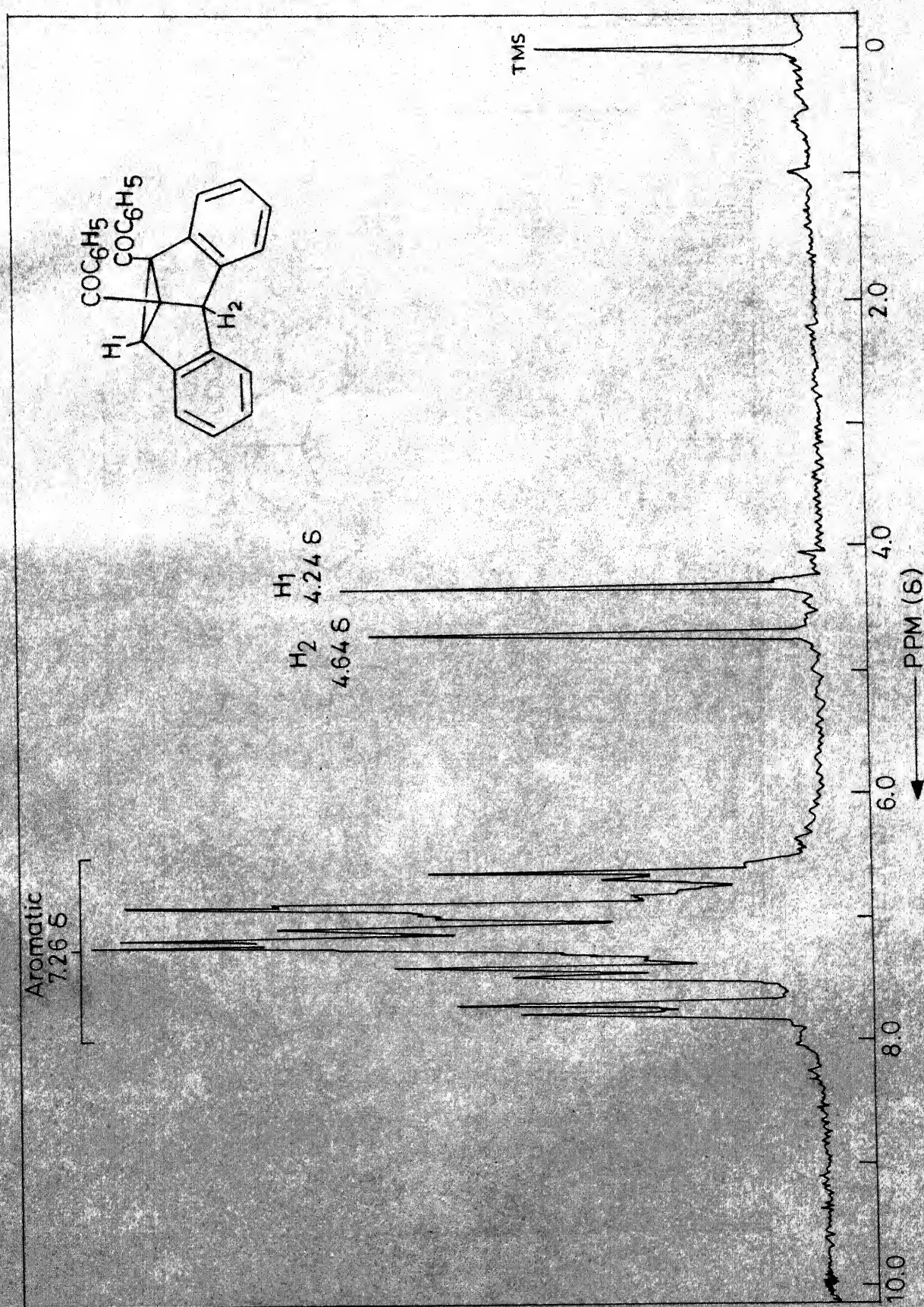


Fig. II. 14 NMR spectrum (100 MHz) of 1,2-dibenzoylbicyclo[3.3.0.0<sup>2,8</sup>]octadiene (63)

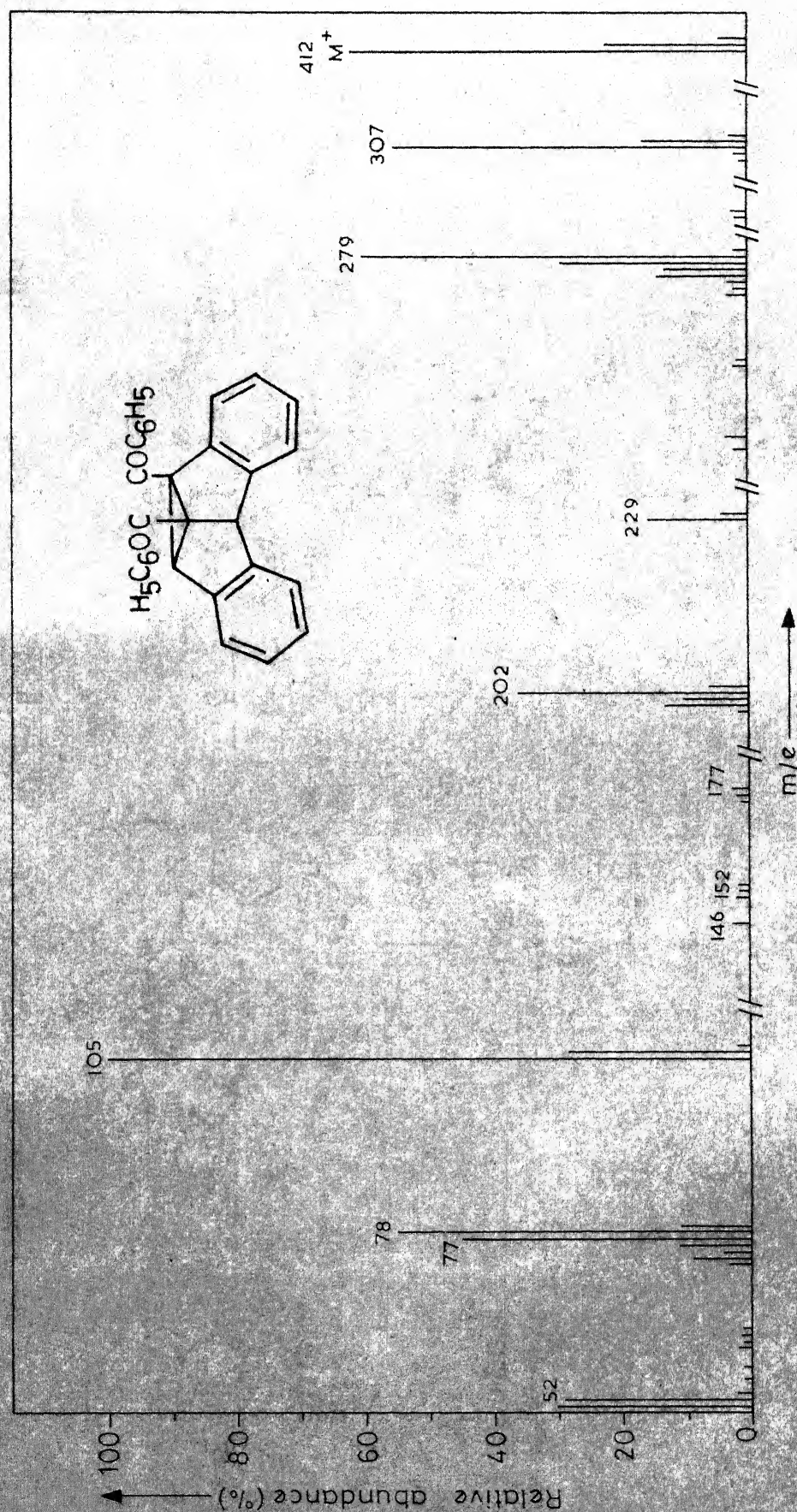
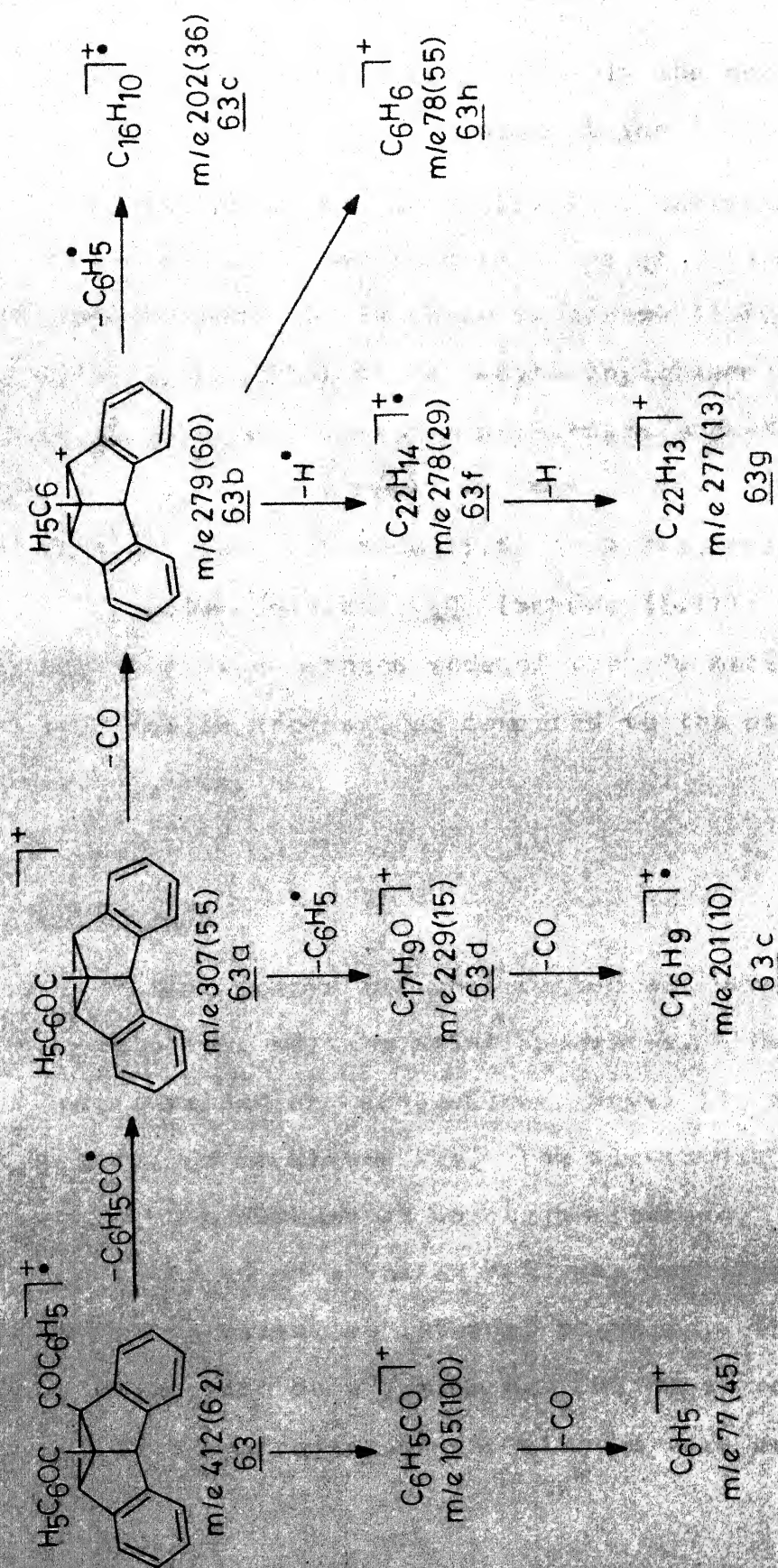


Fig. II.15 Mass spectrum of 1,2-dibenzoyldibenzotricyclo[3.3.0.0<sup>2,8</sup>]octadiene(63)



Scheme II. 21



at  $m/e$  229. The highest intensity peak in the spectrum was observed at  $m/e$  105 due to a benzoyl ion.

The formation of the semibullvalene derivative 63 from 60 can be easily understood in terms of a di- $\pi$ -methane rearrangement, as is shown in Scheme II.20. It is pertinent to observe that the cis-dibenzoylalkene moiety present in 60 does not undergo a photo-rearrangement analogous to the one observed in the case of dibenzoyl ethylenes (Scheme II.5) or 2,3-dibenzoyl-bicyclo[2.2.2]octa-2,5-diene (20) (Scheme II.11). It appears that the di- $\pi$ -methane mode of transformation of 60 is a more facile process, as compared to the other rearrangement mode.

#### II.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. The infrared spectra were recorded on Perkin-Elmer, Model 137 and Model 521 Infrared Spectrometers. The electronic spectra were recorded on a Beckman DB Spectrophotometer. Nmr traces were recorded on a Varian A-60 Nmr Spectrometer, using tetramethyl-silane as internal standard. The mass spectra were recorded on a Varian Mat CH7 Mass Spectrometer at 70 eV. All the irradiation experiments were carried



out either in a 150W Srinivasan-Griffin-Rayonet Photochemical Reactor (3500 Å) or by using a Hanovia 450W, medium pressure mercury lamp in a quartz-jacketed immersion well.

#### II.4.1 Starting Materials

2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (18), 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (20), 6,7-dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene (37), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (47) and 9,10-dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (60) were prepared by reported procedures.<sup>41</sup> Dry benzene and absolute methanol were used for photolysis experiments. Petroleum ether used was the fraction, bp 60-80°.

#### II.4.2 Photolysis of 2,3-Dibenzoylbicyclo[2.2.1]hepta-2,5-diene (18)

A solution of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (500 mg, 1.67 mmol) in benzene (160 ml) was irradiated in a 150W-Srinivasan-Griffin-Rayonet Photochemical Reactor for 1 hr. The solvent was removed under vacuum and the residue was recrystallized from a mixture (2:1) of petroleum ether and benzene to give 450 mg (90%) of white, needle-shaped crystals of 2,3-dibenzoylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (19), mp 151-152°.

Anal. Calcd for  $C_{21}H_{16}O_2$ : C, 84.0; H, 5.33; Mol. wt., 300. Found: C, 83.83; H, 5.70; Mol. wt., 300 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ :  $3065\text{ cm}^{-1}$  ( $\nu_{C-H}$ ), 2935 and  $2865\text{ cm}^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric),  $1660\text{ cm}^{-1}$  ( $\nu_{C=O}$ ).

UV spectrum (Ethanol)  $\lambda_{\max}$ : 243 nm ( $\epsilon$ , 24,550), 280 (4,000).

#### II.4.3 Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (20)

A solution of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (575 mg, 2.46 mmol) in benzene (210 ml) was photolysed for  $3\frac{1}{2}$  hr, under a 450W Hanovia medium pressure mercury lamp, provided with a pyrex filter. The photolysis was repeated several times to photolyse 2.3 g (0.01 mol) of 20. Removal of the solvent from the photolysed mixture gave a residual solid, which was chromatographed over silica-gel. Elution of the column with petroleum ether gave 100 mg of biphenyl, mp  $69-70^\circ$  (mixture mp).

Further elution with a mixture (50:1) of petroleum ether and benzene gave 350 mg (23%) of the lactone, 23, mp  $139-140^\circ$ , after recrystallization from a mixture (5:1) of petroleum ether and benzene.

Anal. Calcd for  $C_{22}H_{18}O_2$ : C, 84.07; H, 5.73;  
Mol. wt., 314. Found: C, 84.35; H, 5.65; Mol. wt., 314  
(Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3045, 2955 and 2945  $\text{cm}^{-1}$   
( $\nu_{C-H}$ ), 2925 and 2865  $\text{cm}^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric),  
1771  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1666 and 1596  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 224 nm ( $\epsilon$ , 5,500),  
240 (4,400) and 260 (2,500).

Further elution of the column with a mixture (20:1)  
of petroleum ether and benzene gave 800 mg (35%) of the  
starting material (20), mp 153° (mixture mp), after  
recrystallization from a mixture (2:1) of petroleum ether  
and benzene.

Continued elution of the column with a mixture  
(1:1) of petroleum ether and benzene gave 400 mg (26%) of  
6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-  
5-exo-carboxylic acid (21), mp 293°, after crystallization  
from a mixture (2:1) of petroleum ether and benzene.

Anal. Calcd for  $C_{22}H_{20}O_3$ : C, 79.50; H, 6.02;  
Mol. wt., 332. Found: C, 79.71; H, 5.63; Mol. wt., 332  
(Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3035, 2935 and 2895  $\text{cm}^{-1}$   
( $\nu_{C-H}$ ), 2945 and 2845  $\text{cm}^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric),  
1710  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1650, 1600 and 1590  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 229 nm ( $\epsilon$ , 12,000) and 260 (14,500).

Subsequent elution of the column with a mixture (1:2) of petroleum ether and benzene gave 100 mg (6%) of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-endo-carboxylic acid (22), mp 269°, after recrystallization from a mixture (2:1) of petroleum ether and benzene.

Anal. Calcd for  $C_{22}H_{20}O_3$ : C, 79.50; H, 6.02; Mol. wt., 332. Found: C, 79.45; H, 6.10; Mol. wt., 332 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3045, 2977, 2915 and 2885  $cm^{-1}$  ( $\nu_{C-H}$ ), 2935 and 2835  $cm^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric), 1715  $cm^{-1}$  ( $\nu_{C=O}$ ), 1668, 1600 and 1590  $cm^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 226 nm ( $\epsilon$ , 13,200) and 260 (11,000).

#### II.4.4 Esterification of 6-(1-Phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylic acid (21)

Through an ice-cold solution of 21 (99 mg, 0.3 mmol) in ether (25 ml), diazomethane was passed till the mixture became distinctly yellow in colour. The mixture was kept at 0° for 3 hr and later the solvent was removed

under vacuum to give a residual solid. Recrystallization of this product from a mixture (9:1) of petroleum ether and benzene gave 60 mg (57%) of methyl-6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylate (24), mp 131°.

Anal. Calcd for  $C_{23}H_{22}O_3$ : C, 79.76; H, 6.41.  
Found: C, 80.05; H, 6.36.

Ir spectrum (KBr)  $\nu_{\max}$ : 3080  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ) and 1750  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ).

Nmr spectrum ( $\text{CDCl}_3$ ): 1.51 $\delta$  (m, 2H,  $\text{CH}_2$ ), 1.88 $\delta$  (m, 2H,  $\text{CH}_2$ ), 2.92 $\delta$  (m, 1H, bridge-head proton), 3.31 $\delta$  (m, 1H, tertiary endo-proton, attached to the carbon atom bearing the carbomethoxy group), 3.43 $\delta$  (s, 3H,  $\text{OCH}_3$ ), 3.58 $\delta$  (m, 1H, bridge-head proton) and 6.80 $\delta$  (complex multiplet, 12H, vinylic and aromatic protons).

#### II.4.5 Esterification of 6-(1-Phenoxy-1-phenylmethylene)-bicyclo[2.2.2]oct-2-ene-5-endo-carboxylic acid (22)

Through a solution of 22 (66 mg, 0.2 mmol) in ether (20 ml), diazomethane was passed till the solution became yellow in colour. The reaction mixture was kept at 0° for 3 hr. Removal of the solvent under vacuum and recrystallization of the residue from a mixture (9:1) of petroleum ether and benzene gave 30 mg (43%) of the

methyl 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-endo-carboxylate (25), mp 125°.

Ir spectrum (KBr)  $\nu_{\max}$ : 3100  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ) and 1760  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ),

Nmr spectrum ( $\text{CDCl}_3$ ): 1.39 $\delta$  (m, 2H,  $\text{CH}_2$ ), 1.63 $\delta$  (m, 2H,  $\text{CH}_2$ ), 2.92 $\delta$  (m, 1H, bridge-head proton), 3.38 $\delta$  (s, 3H,  $\text{OCH}_3$ ), 3.47 $\delta$  (d, 1H, tertiary exo-proton attached to the carbon atom bearing the carbomethoxy group), 3.62 $\delta$  (m, 1H, bridge-head proton) and 6.83 $\delta$  (m, 12H, aromatic and vinylic protons).

#### II.4.6 Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (20) in Methanol

A solution of 20 (250 mg, 0.75 mmol) in absolute methanol (160 ml) was photolysed in a Srinivasan-Griffin-Rayonet Photochemical Reactor for 5 hr. In several repeat runs, a total of 750 mg of 20 was photolysed and the combined mixture was worked up by chromatographing over a neutral alumina column.

Elution of the column with petroleum ether gave 300 mg (69%) of methyl 6-(1-phenoxy-1-phenylmethylene)-bicyclo[2.2.2]oct-2-ene-5-exo-carboxylate (24), mp 130° (mixture mp), after recrystallization from a mixture (9:1) of petroleum ether and benzene.

Further elution of the column with petroleum ether gave 5 mg (1%) of methyl 6-(1-phenoxy-1-phenylmethylene)-bicyclo[2.2.2]oct-2-ene-5-endo-carboxylate (25), mp 125° (mixture mp), after recrystallization from a mixture (9:1) of petroleum ether and benzene.

Subsequent elution of the column with a mixture (10:1) of petroleum ether and benzene gave 350 mg (47%) of the unchanged starting material (20), mp 153° (mixture mp).

II.4.7 Photolysis of 6,7-Dibenzoyltricyclo[3.2.2.0<sup>2,4</sup>]-nona-6,8-diene (37)

A solution of 37 (652 mg, 2 mmol) in benzene (210 ml) was irradiated for 2½ hr, using a 450W Hanovia medium pressure mercury lamp fitted with a pyrex filter and under nitrogen atmosphere. The procedure was repeated five times to photolyse a total amount of 3.26 g (10 mmol) of 37. Removal of the solvent from the combined photolyzed mixture gave a residue which was chromatographed over silica-gel. Elution of the column with a mixture (19:1) of petroleum ether and benzene gave 480 mg (33%) of white crystals of the lactone, 40, mp 128°, after recrystallization from a mixture (8:1) of petroleum ether and benzene.



Anal. Calcd for  $C_{23}H_{18}O_2$ : C, 84.66; H, 5.52;  
Found: C, 85.10; H, 5.41.

Ir spectrum (KBr)  $\nu_{\max}$ : 3045, 2980, 2970, 2905  
and  $2880\text{ cm}^{-1}$  ( $\nu_{C-H}$ ),  $1770\text{ cm}^{-1}$  ( $\nu_{C=O}$ ) and  $1040\text{ cm}^{-1}$   
( $\nu_{CH_2}$ , wagging).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 230 nm ( $\epsilon$ , 5,000),  
242 (3,500) and 260 (2,500).

Further elution of the column with benzene gave  
1.8 g (55%) of the starting material (37), mp  $133^\circ$  (mixture  
mp), after recrystallization from a mixture (3:1) of  
petroleum ether and benzene.

#### II.4.8 Photolysis of 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]- hepta-2,5-diene (47)

A solution of 47 (500 mg, 1.6 mmol) in benzene  
(250 ml) was irradiated by using 450W Hanovia medium  
pressure mercury lamp, for  $2\frac{1}{2}$  hr, under nitrogen atmos-  
phere. The procedure was repeated several times to  
photolyse a total amount of 2.5 g of the starting material.  
Removal of the solvent from the combined photolysates gave  
a product which was chromatographed over silica-gel.  
Elution with petroleum ether gave 50 mg of biphenyl,  
mp  $69-70^\circ$  (mixture mp). Continued elution with a mixture  
(20:1) of petroleum ether and benzene gave 250 mg (13%)  
of dibenzoylacetylene, mp  $110-111^\circ$  (mixture mp).

Further elution with a mixture (1:1) of petroleum ether and benzene gave 800 mg (32%) of 1,5-dibenzoyl-5-formyl-1,3-cyclopentadiene, (50), mp 172°d, after recrystallization from a mixture (5:1) of cyclohexane and benzene.

Anal. Calcd for  $C_{20}H_{14}O_3$ : C, 79.47; H, 4.63; Mol. wt., 302. Found: C, 79.66; H, 4.45; Mol. wt., 302 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3120 and 2870  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1675  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1600 and 1575  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 244 nm ( $\epsilon$ , 16,000), 268 (19,000), 298 (19,500) and 360 (6,400).

#### II.4.9 Photolysis of 9,10-Dihydro-11,12-dibenzoyl-9,10-ethenoanthracene (60)

A solution of 60 (400 mg, 1 mmol) in benzene (200 ml) was irradiated by using a 450W Hanovia medium pressure mercury lamp for 4 hr, under nitrogen atmosphere. Removal of the solvent and recrystallization of the residue from a mixture (1:1) benzene and hexane gave 350 mg (88%) of white crystals of 1,2-dibenzoyldibenzotricyclo[3.3.0.0<sup>2,8</sup>]-octadiene (63), mp 183°.

Anal. Calcd for  $C_{30}H_{20}O_2$ : C, 87.38; H, 4.85. Mol. wt., 412. Found: C, 87.52; H, 5.10; Mol. wt., 412 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3065, 3015, and 2955  $\text{cm}^{-1}$   
( $\nu_{\text{C-H}}$ ), 1675 and 1665  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1595 and 1580  $\text{cm}^{-1}$   
( $\nu_{\text{C=C}}$ ).

UV spectrum (Ethanol)  $\lambda_{\max}$ : 230 nm ( $\epsilon$ , 25,000),  
250 (29,500), 279 (7,600) and 324 (700).

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## CHAPTER III

### PREPARATION OF ENAMINE DIONES BY THE ADDITION OF NUCLEOPHILES TO DIBENZOYLACETYLENE

#### III.1 ABSTRACT

Several enamine diones have been prepared through the nucleophilic addition of different amines to dibenzoylacetylene (DBA). Thus, the reaction of aniline, piperidine, *o*-aminophenol and N-phenylbenzylamine with DBA gave the corresponding 1:1-adducts namely, 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5), 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6), 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (7) and 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione (8). Uv absorption data reveal that the adducts 5 and 7, formed from aniline and *o*-aminophenol, respectively, are the E-isomers, arising through a trans-mode



of addition, whereas the adducts 6 and 8, formed from piperidine and N-phenylbenzylamine are the Z-isomers, formed through a cis-mode of addition.

The reaction of N-phenacylaniline with DBA gave 2,3-dibenzoyl-1,4-diphenylpyrrole (11), whereas o-phenylenediamine reacts with DBA to give 2-(2-hydroxy-2-phenylethene)-3-phenylquinoxaline (22). The quinoxaline derivative 22, on treatment with bromine in carbon tetrachloride gave 2-bromophenacyl-3-phenylquinoxaline (23), whereas, nickel peroxide oxidation of 22 leads to the formation of an oxidative dimer, namely, 1,4-diphenyl-2,3-bis(3-phenylquinox-2-yl)butane-1,4-dione (26).

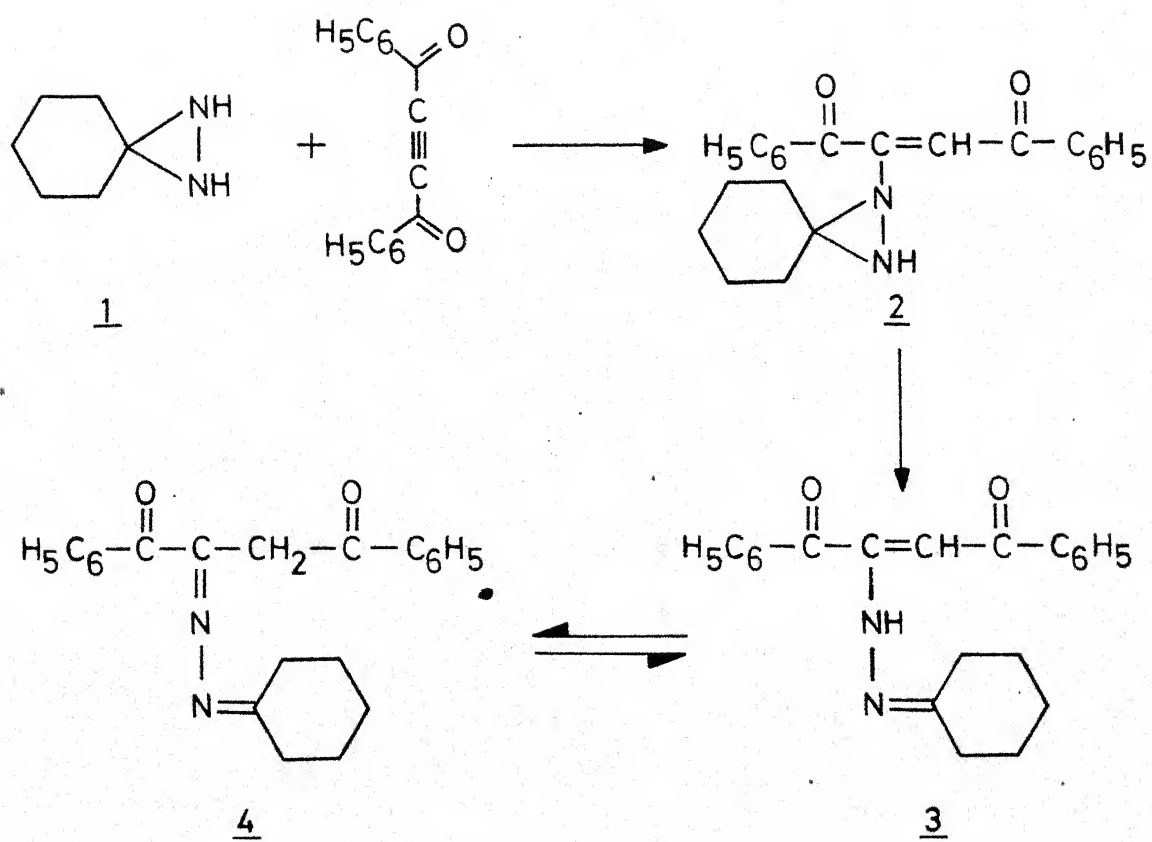
The reaction of 1,8-diaminonaphthalene with DBA gave a mixture of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine (32) and 2-benzoylperimidine (33), whereas reaction of 2-aminopyridine with DBA gave a mixture of two 1:1-adducts, 2-(2-imino-1(2H)pyridyl)-1,4-diphenylbut-2-ene-1,4-dione (34) and 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35).

Electron-impact induced transformation of the adducts 5, 6, 7, 8, 11 and 35 revealed that the Z-isomers 6, 8 and 11, undergo a slightly different mode of fragmentation as compared to the E-isomers, 5, 7 and 35.

### III.2 INTRODUCTION

Several examples of nucleophilic addition to acetylenic ketones are reported in the literature.<sup>1</sup> Nitrogen-containing nucleophiles like ammonia and amines, in general, add to acetylenic ketones to give simple 1:1-adducts consisting of  $\alpha,\beta$ -unsaturated- $\beta$ -aminoketones.<sup>2-20</sup> The reaction of a few primary and secondary amines with dibenzoylacetylene (DBA), for example, has been studied by Du Pont, who has shown that enamine diones are formed very readily in these cases.<sup>17</sup> In a recent investigation, Heine et al.<sup>21</sup> have shown that diaziridines react with DBA at ambient temperatures to give the corresponding 2-(alkyldenehydrazino)-1,4-diphenyl-2-butene-1,4-diones, arising through a Michael type of addition reaction. In the reaction of 3,3-pentamethylenediaziridine (1), for example, the initially formed adduct 2, undergoes facile conversion to the enamine adduct 3, which then gradually isomerizes to the imine form 4 (Scheme III.1). No detailed study concerning the stereochemistry of amine additions to DBA has been reported in the literature. McMullen and Stirling<sup>16</sup> have examined the reaction of some primary and secondary amines to few monoaryl ethylenic ketones and have observed that secondary amines give rise to enamines with E-configuration, whereas, the reaction of primary amines leads to an equilibrium mixture of adducts,

Scheme III.1



consisting of E- and Z-isomers. Further, it has been observed that the ratio of Z- to E-isomers in these reactions depend on several factors like the nature of the amine and the solvent employed.

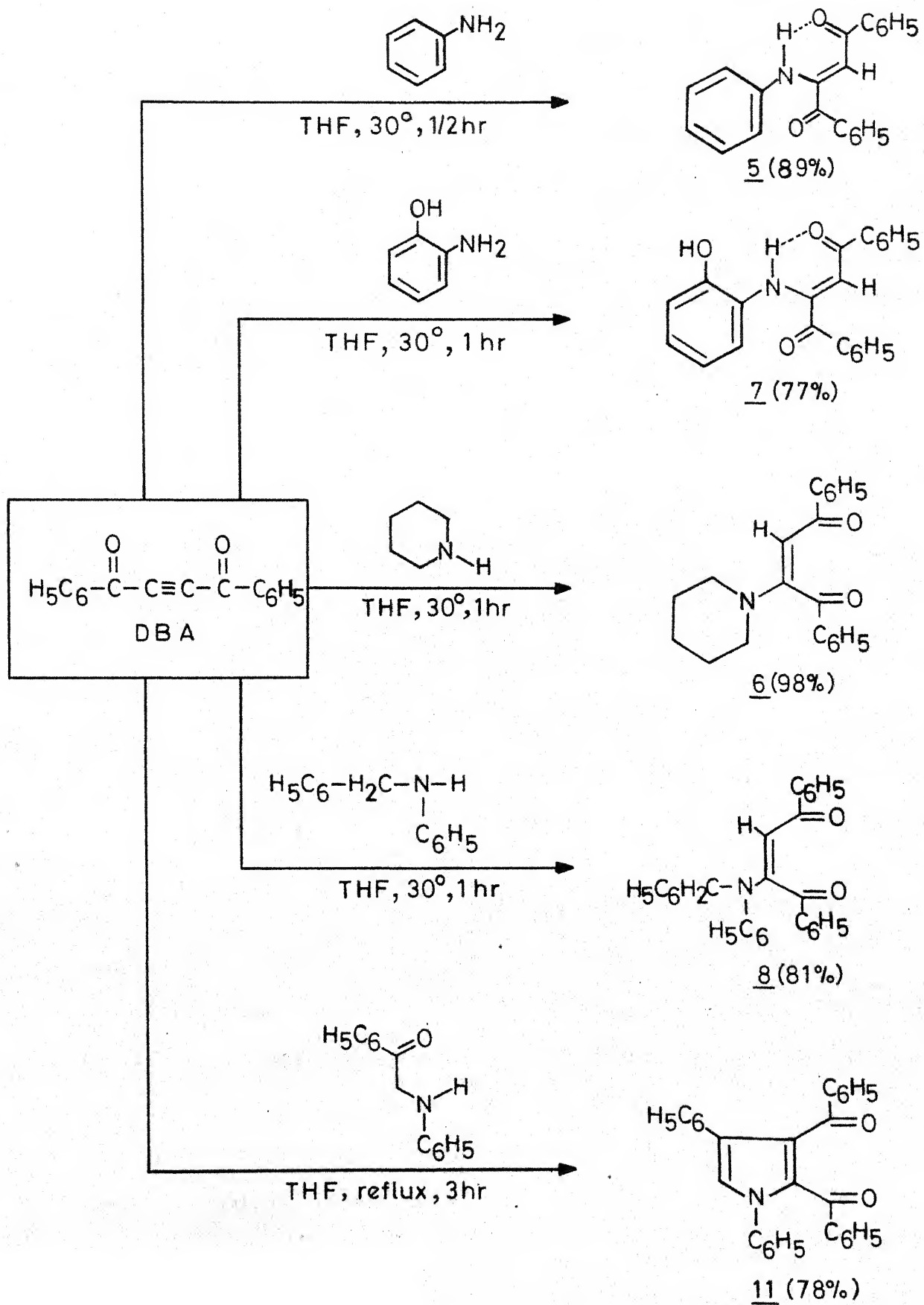
The object of the present investigation has been to study the reaction of a few monofunctional and bifunctional nitrogen-containing nucleophiles with DBA, with a view to using these reactions for the synthesis of different 1,2-dibenzoylalkenes and also to examine the stereochemistry of some of these addition reactions. In this connection, we have examined the reactions of aniline, piperidine, N-phenylbenzylamine, *o*-aminophenol, N-phenacylaniline, *o*-phenylenediamine, 1,8-diaminonaphthalene and 2-aminopyridine with DBA.

### III.3 RESULTS AND DISCUSSION

#### III.3.1 Synthesis of Enamine Diones

The reaction of aniline and piperidine with DBA has been reported earlier to give the corresponding 1:1-addition products.<sup>17,19</sup> In the present studies, we have reinvestigated these reactions with a view to examining the stereochemistry of these additions and also the electron-impact induced transformation of the corresponding adducts.

Treatment of a mixture of aniline with DBA in tetrahydrofuran, for example, gave a 89% yield of a product,



identified as 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5) (Scheme III.2). The nmr spectrum of 5 (Fig. III.1) showed a singlet at  $6.3\delta$  (1H), multiplets centred around  $7.26\delta$  (5H),  $7.7\delta$  (6H) and  $8.12\delta$  (4H) and a broad singlet at  $12.75\delta$  (1H). Of these, the sharp singlet at  $6.3\delta$  is assigned to the olefinic proton, whereas the broad singlet at  $12.75\delta$  which is exchangeable with  $D_2O$  is assigned to the NH proton. Of the three multiplets, the one at  $7.26\delta$  is assigned to the phenyl protons of the aniline nucleus, as one would expect these protons to appear at a higher field due to the electron-donating ability of the amine function. The multiplet at  $8.12\delta$  is assigned to the ortho protons of the two benzoyl groups, whereas the multiplet at  $7.7\delta$  is assigned to the remaining protons at the meta and para positions of the benzoyl groups.

Similarly, the reaction of piperidine with DBA gave a 98% yield of 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6). The nmr spectrum of 6 (Fig. III.2) showed signals at  $1.67\delta$  (6H) and  $3.35\delta$  (4H) for the methylene protons of the piperidine nucleus. Of these, the down-field signal at  $3.35\delta$  is attributed to the methylene protons adjacent to the nitrogen atom, whereas, the signal at  $1.67\delta$  is attributed to the remaining methylene protons. The olefinic proton appeared as a singlet at  $6.13\delta$  and the

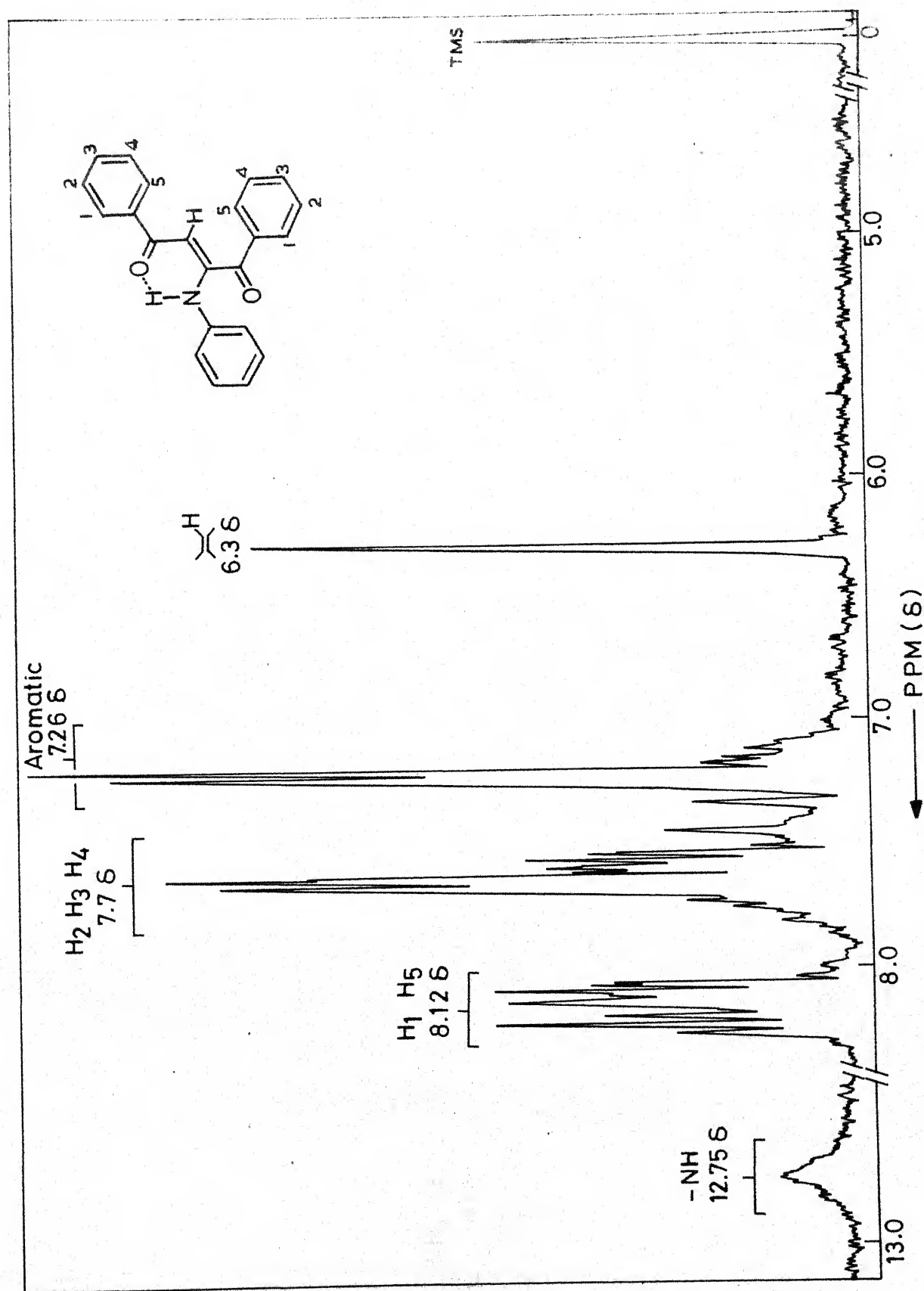


Fig. III.1 NMR spectrum (60 MHz) of 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5)



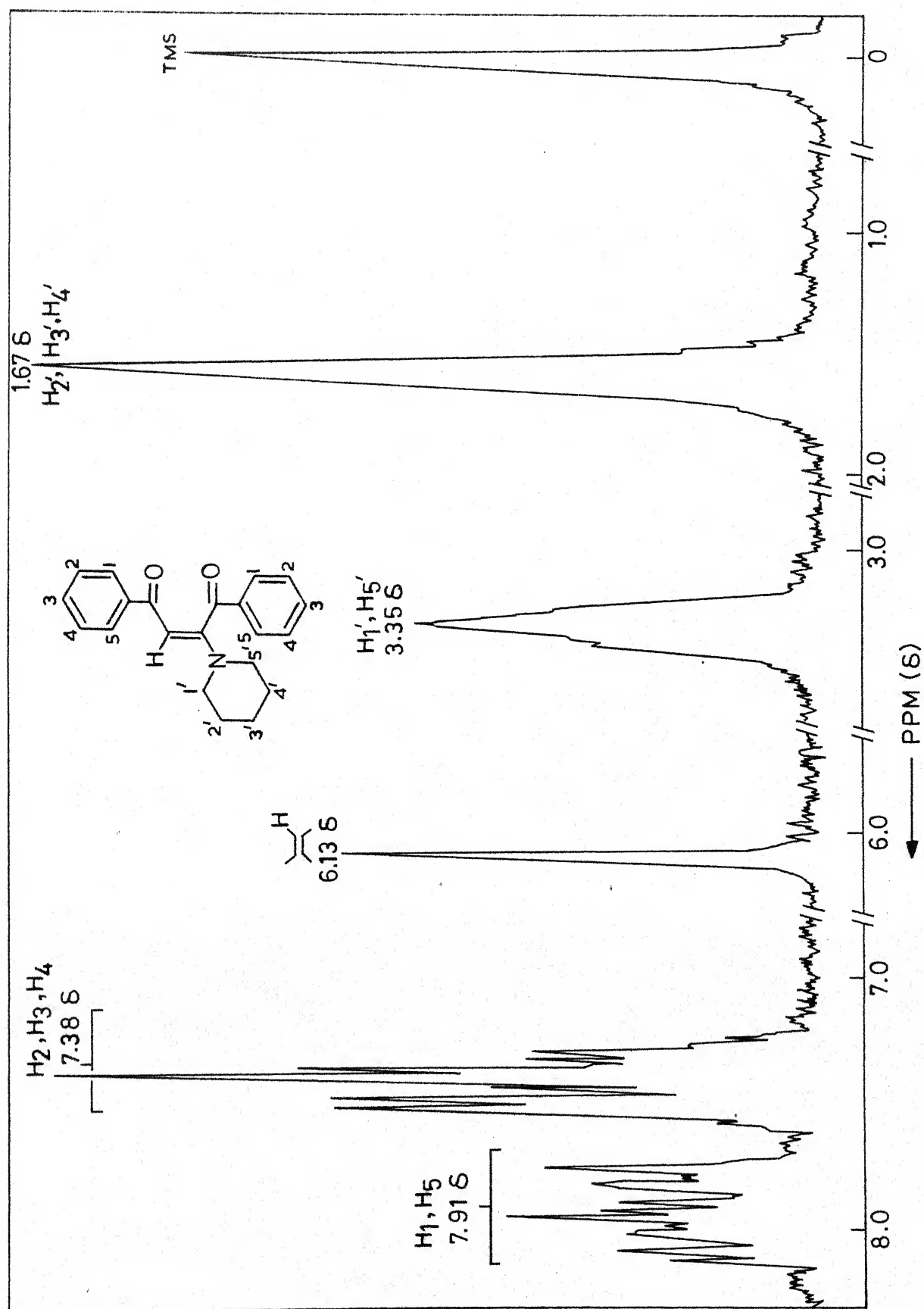


Fig. III.2 NMR spectrum (60 MHz) of 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6)

benzoyl protons appeared as two sets of multiplets at 7.38  $\delta$  (6H) and 7.91  $\delta$  (4H), respectively.

The reaction of a bifunctional nucleophile like *o*-aminophenol with DBA gave a 77% yield of a 1:1-adduct, identified as 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (7). The structure of 7 was confirmed on the basis of elemental analysis and spectral evidences. The nmr spectrum of 7 (Fig. III.3) showed a singlet at 5.82  $\delta$  (1H) which is assigned to the vinylic proton. Two other singlets were observed at 6.45  $\delta$  (1H) and 12.88  $\delta$  (1H), which were exchangeable with D<sub>2</sub>O and these are assigned to the OH and NH protons, respectively. The aromatic protons of the two benzoyl groups in 7 appeared as two multiplets at 7.35  $\delta$  (6H) and 7.72  $\delta$  (4H), respectively, whereas the phenyl protons of the amine nucleophile appeared as a multiplet at a higher field namely, 6.98  $\delta$  (4H).

The reaction of a secondary amine like N-phenylbenzylamine with DBA gave a 81% yield of a 1:1-adduct, identified as 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione (8). The nmr spectrum of 8 (Fig. III.4) showed a singlet at 4.77  $\delta$  (2H), assigned to the methylene protons and a second singlet at 6.05  $\delta$  (1H) assigned to the vinylic proton. The aromatic protons appeared as groups of multiplets centered around 7.18  $\delta$  (10H), 7.42  $\delta$  (6H) and 7.85  $\delta$  (4H), respectively.

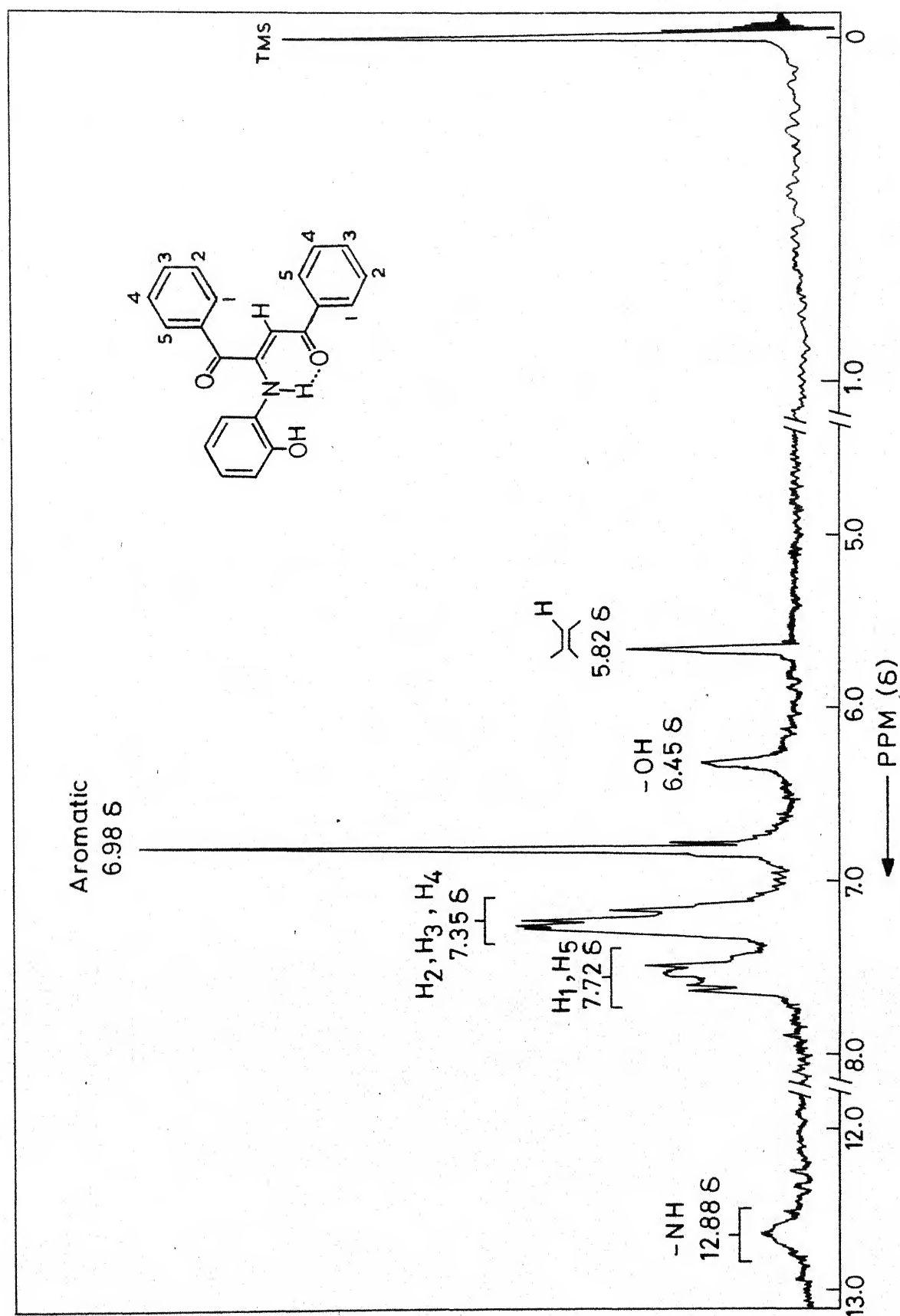


Fig.III.3 NMR spectrum(60MHz) of 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione(7)

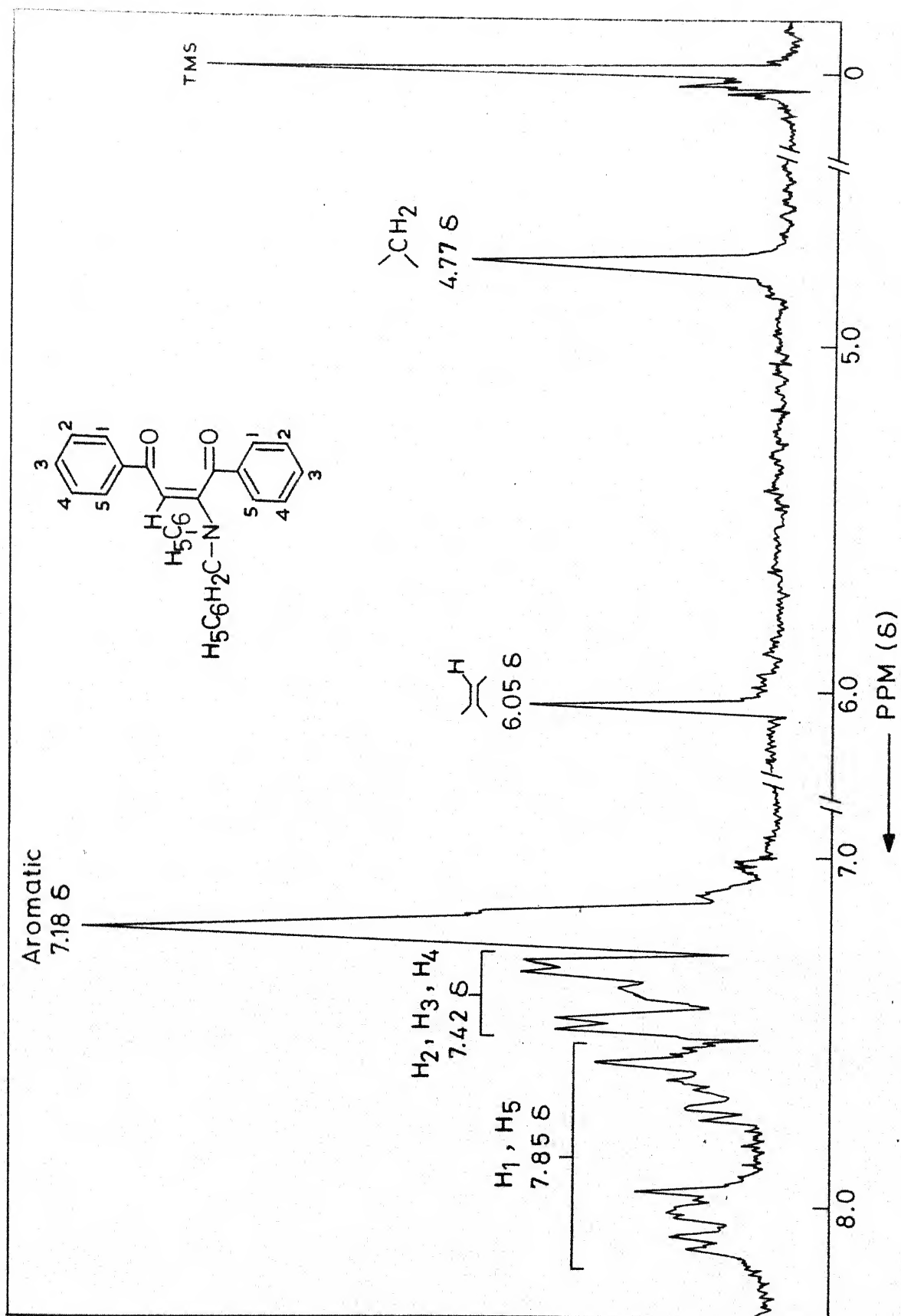
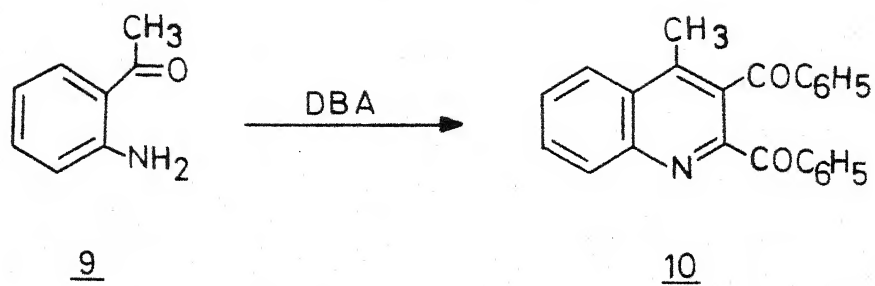


Fig. III. 4 NMR spectrum (60 MHz) of 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione(8)

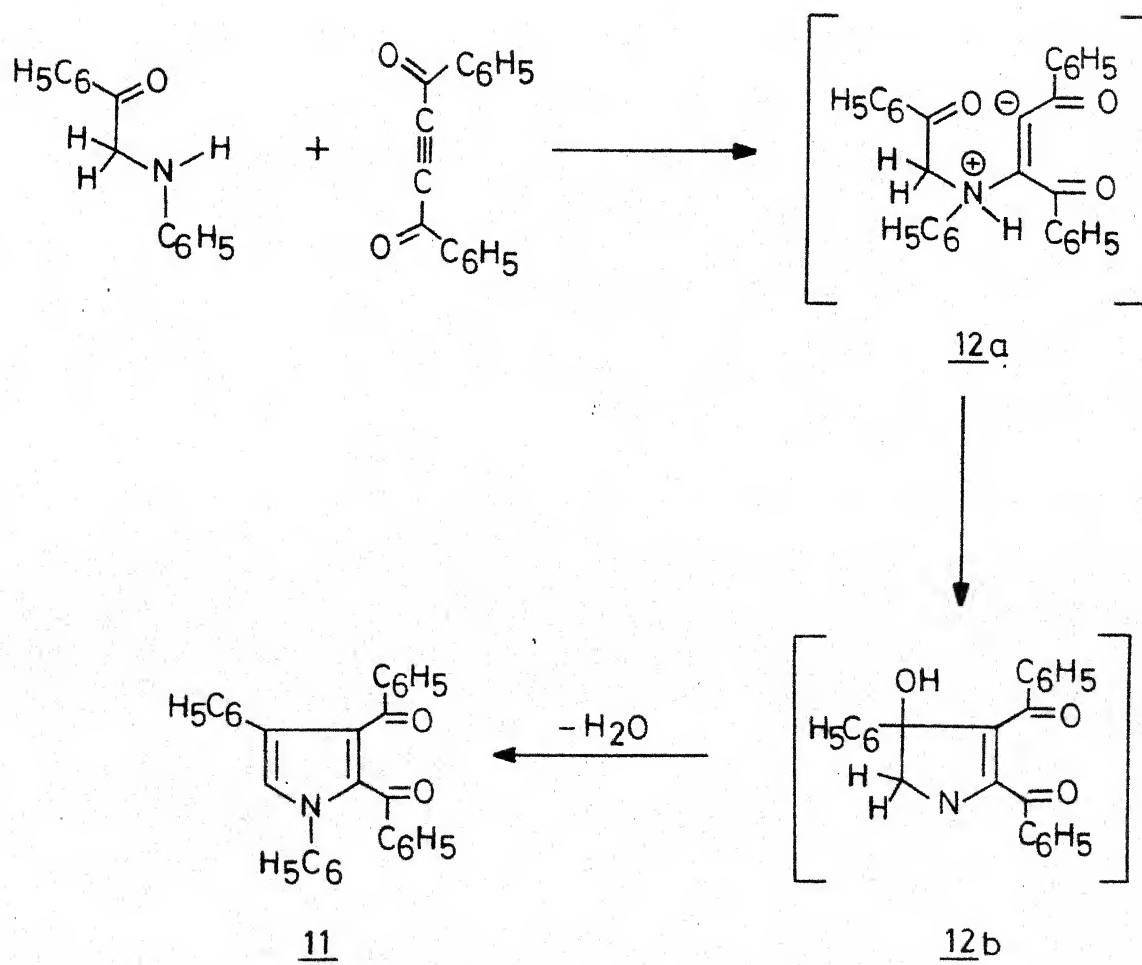
Potts and Elliott<sup>22</sup> have shown that the reaction of nucleophiles containing suitably positioned carbonyl function, with DBA could provide a convenient route to synthesizing heterocyclic compounds. Thus, for example, the reaction of o-aminoacetophenone (9) with DBA gave 2,3-dibenzoyl-4-methylquinoline (10) (Scheme III.3). We have examined the reaction of N-phenacylaniline with DBA with a view to studying the nature of products formed in this reaction. Refluxing of a mixture of N-phenacylaniline and DBA in THF, gave a 78% yield of a product identified as 2,3-dibenzoyl-1,4-diphenylpyrrole (11). The structure of 11 was confirmed on the basis of analytical results and spectral data. The nmr spectrum of 11, for example, showed a multiplet around 7.3 $\delta$ , assigned to the aromatic protons. It might be pointed out in this connection that the reaction of N-phenacylaniline with dimethyl acetylenedicarboxylate (DMAD) is known to give an analogous pyrrole derivative namely, dimethyl 1,4-diphenylpyrrole-2,3-dicarboxylate.<sup>23</sup>

The formation of 11 in this reaction is rationalized in terms of the addition of N-phenacylaniline to DBA giving rise to an intermediate 12a, which can undergo cyclization leading to the pyrroline derivative 12b. Loss of water from the intermediate 12b will result in the formation of the pyrrole derivative 11 (Scheme III.4).

Scheme III. 3



Scheme III. 4

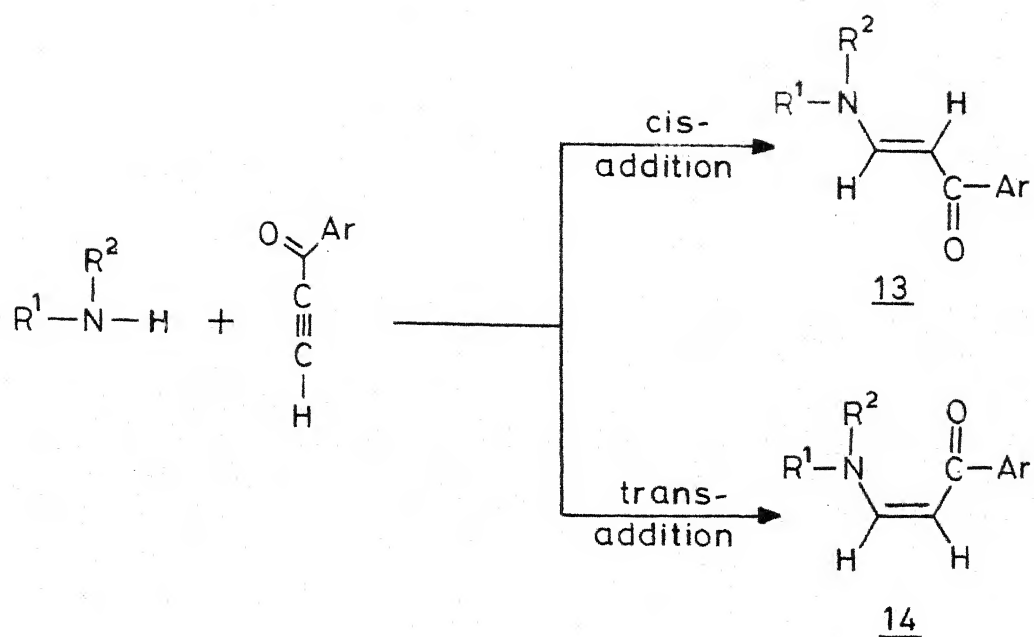


### III.3.2 Stereochemistry of the Addition of Amines to Dibenzoylacetylene

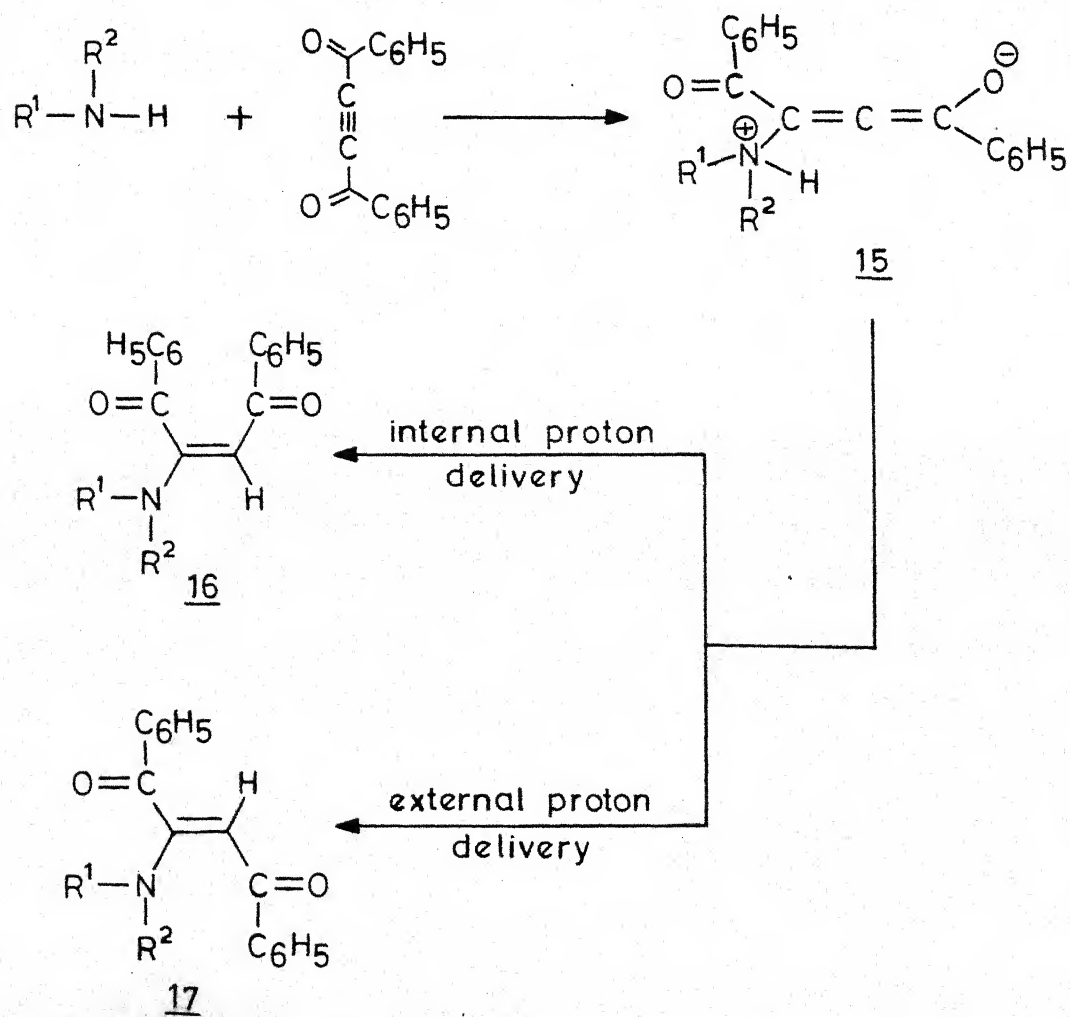
Detailed studies of the stereochemistry of amine additions to acetylenic esters have been carried out by several groups of workers.<sup>24-27</sup> Huisgen and coworkers<sup>25-27</sup> have shown that in the case of primary amines, for example, enamine fumarates, which are thermodynamically more stable than the corresponding maleate isomers, are formed. Thus, in the reaction of aniline with dimethyl acetylenedicarboxylate, the exclusive formation of dimethyl anilino fumarate has been observed. In the case of secondary amines, however, the addition leads to a mixture of enamine maleates and fumarates, depending upon several factors like the nature of the attacking nucleophile, the relative ease of isomerization of the products and also the nature of the solvent used for these reactions.

No detailed study of the stereochemistry of the addition of amines to DBA is reported in the literature. McMullen and Stirling<sup>16</sup> have studied the addition of a few primary and secondary amines to monoaroyl acetylenic ketones and have shown that the trans-enamines (13), arising through a cis-mode of addition are formed in the case of secondary amines, whereas, in the case of primary amines, a mixture of both cis- and trans-addition products are formed (Scheme III.5).





Scheme III. 6

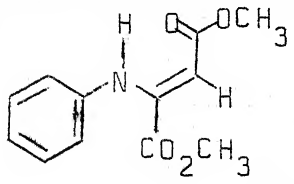
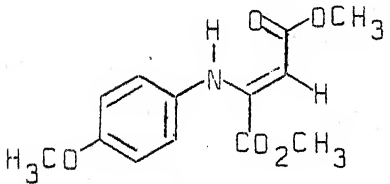
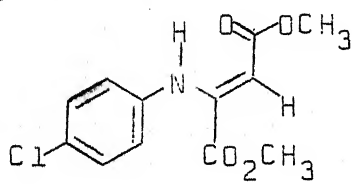
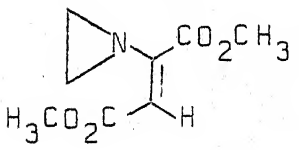
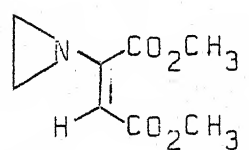
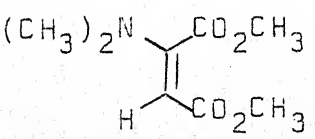
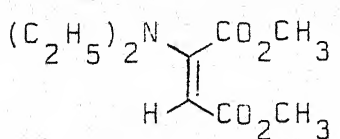
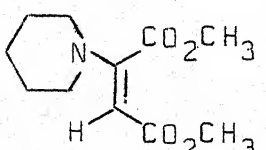


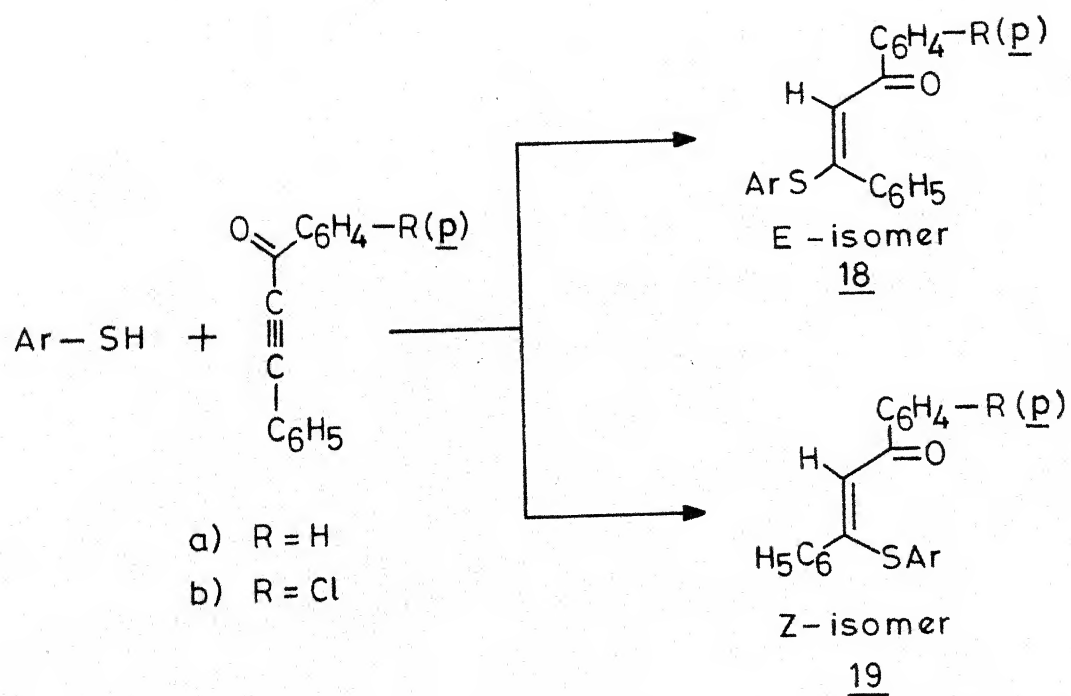
The reaction of an amine nucleophile with DBA would be expected to proceed through a resonance stabilized zwitterionic intermediate, 15, as shown in Scheme III.6. This intermediate in the absence of any external proton source, would undergo a stereospecific collapse, resulting in an internal proton delivery and leading to the formation of a cis-disubstituted alkene derivative, 16. However, in the presence of an external proton source one would expect the formation of the trans-disubstituted alkene derivative, 17, along with that of the cis-isomer. Huisgen and coworkers,<sup>29</sup> in their studies on the addition of amines to acetylenic esters, have shown that in several cases even the excess of attacking nucleophile can serve as the external proton source. In the case of primary amines, an additional factor would be the extra stability of the trans-isomer through intramolecular hydrogen-bonding of the proton attached to the nitrogen nucleophile. Thus, we find that in the addition reactions of aniline and *o*-aminophenol with DBA, the products formed are predominantly of the trans-geometry. However, in the case of secondary amines like piperidine and N-phenylbenzylamine, the addition is assumed to proceed through a cis-mode, resulting in the formation of the corresponding cis-derivatives. It might be pointed out in this connection that unlike in the cases of the enamine maleates and

fumarates, formed from acetylenic esters, the stereochemistry of the amine addition products of DBA cannot be ascertained on the basis of the nmr chemical shifts of the vinylic protons. In the adducts, 5, 6, 7 and 8, that have been obtained in the present studies, the chemical shifts of the vinylic protons have been found to be in the range of 5.82 $\delta$  to 6.30 $\delta$  and no discernable difference has been observed between the chemical shifts of the vinylic protons of the cis-dibenzoylalkene adducts and the trans-dibenzoylalkene adducts. However, our stereochemical assignments for these addition products find support from uv spectral studies.

An examination of the electronic absorption data of a few enamine fumarates and maleates which are reported in the literature (Table III.1) reveals that the enamine maleates are characterized by a strong absorption band around 280 nm. In the case of enamine fumarates, however, this band is shifted to a longer wave length and is generally observed around 320 nm. A similar observation has been made by Omar and Basyouni,<sup>30</sup> in the case of the thiol adducts of acetylenic ketones. These investigators have found that the E-isomers (18), arising through a cis-mode of addition, exhibit longer wave absorption bands as compared to the Z-isomers (19), formed through a trans-mode of addition (Scheme III.7).

Table III.1 - Uv Absorption Data of Some Enamine Fumarates and Maleates

Compound	$\lambda_{\max}$ (nm)	$\epsilon$	Reference
	234 323	9,120 13,800	25
	239 324	9,550 12,300	25
	244 322	9,120 14,450	25
	292	9,800	26
	254	18,600	25
	282	23,440	25
	277	21,000	26
	278	20,500	26

Scheme III.7

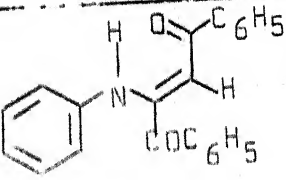
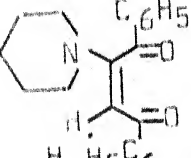
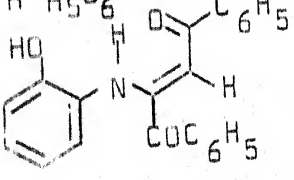
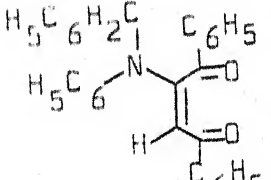
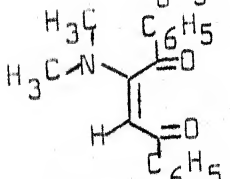
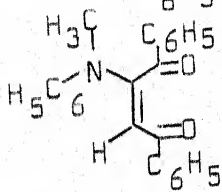
The uv absorption values of some of the enamine diones that we have prepared in the present studies, are listed in Table III.2. It is evident from Table III.2 that the adducts 5 and 7, obtained from the reactions of aniline and o-aminophenol, respectively with DBA, exhibit a bathochromic shift in the longer wavelength absorption band. In contrast, the adducts 6 and 8, obtained from the reactions of piperidine and N-phenylbenzylamine with DBA, show the longer wavelength absorption band around 345-350 nm. It has been reported earlier that the adducts formed from the reactions of dimethylamine and N-methylaniline with DBA also show the presence of such an absorption band around 345 nm (Table III.2).<sup>20</sup>

### III.3.3 Reactions of Bifunctional Amine Nucleophiles with Dibenzoylacetylene

In continuation of our general interest in synthesizing 1,2-dibenzoylalkenes through the addition of nucleophiles to DBA, we have examined the reactions of a few bifunctional nucleophiles like o-phenylenediamine, 1,8-diaminonaphthalene and 2-aminopyridine with DBA.

The reaction of o-phenylenediamine with DBA has been investigated earlier by Bindra and Le Goff,<sup>31</sup> who have shown that 2-benzoyl-4-phenyl-(1H)1,5-benzodiazepine (20) is formed as the major product (Scheme III.8). It

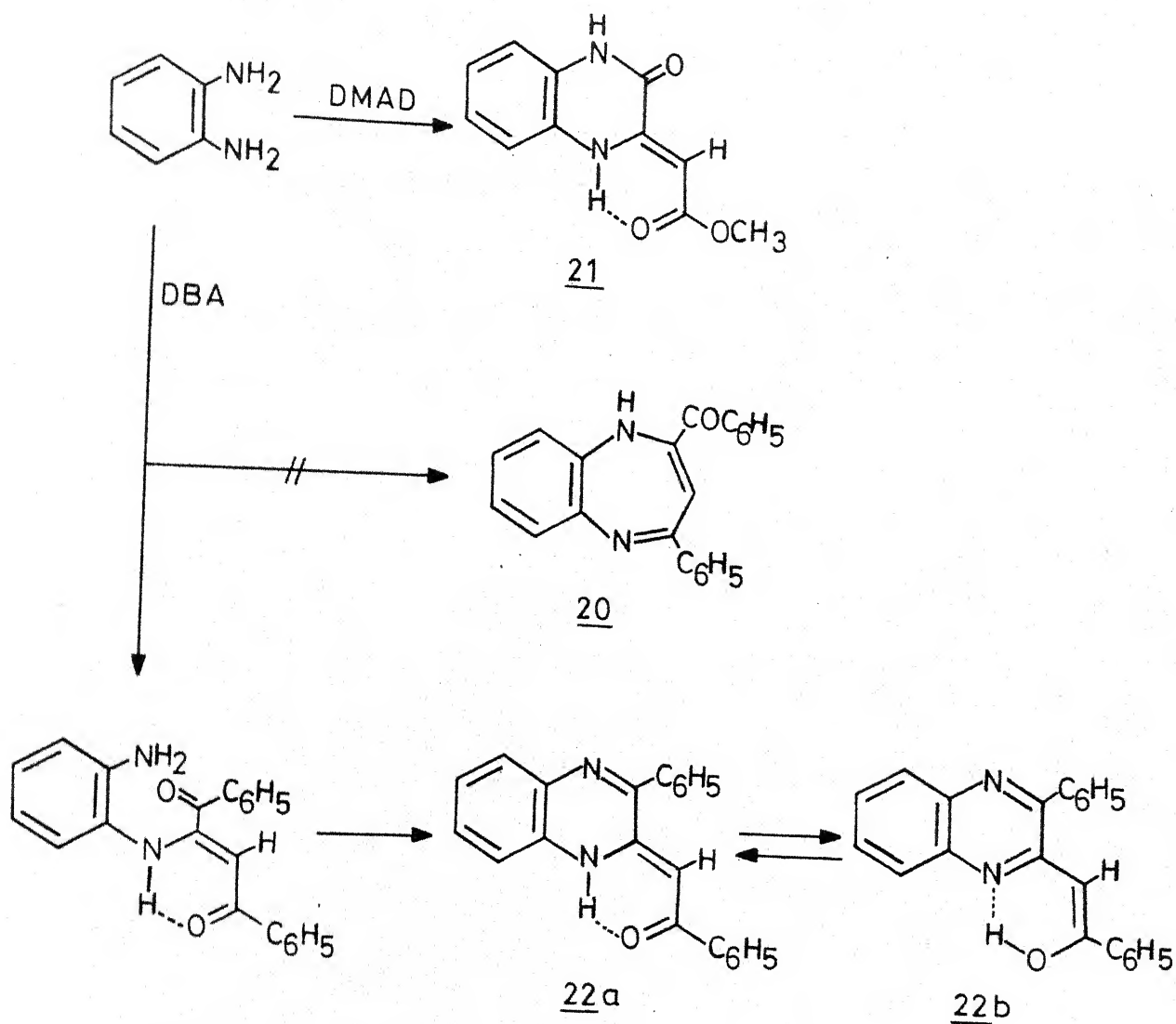
Table III.2 - Uv Absorption Data of Some Enamine Diones

Compound	$\lambda_{\max}$ (nm)	$\epsilon$
 (5)	258 375	22,600 19,000
 (6)	255 350	22,000 20,500
 (7)	260 392	15,000 27,000
 (8)	258 347	22,000 18,600
	254* 350	21,000 17,500
	256* 342	20,800 18,300

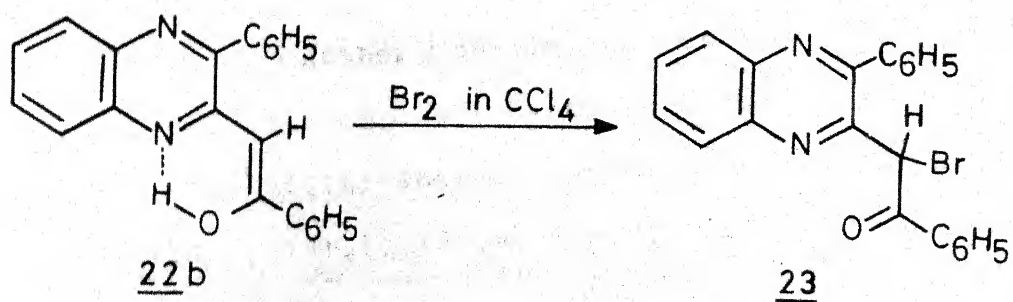
\*See, ref. 20.



Scheme III.8



Scheme III.10



might be mentioned in this connection that the reaction of o-phenylenediamine with dimethyl acetylenedicarboxylate is reported to give a quinoxaline derivative, 2-oxo-3-carbomethoxymethylene-1,2,3,4-tetrahydroquinoxaline (21).<sup>32-35</sup> In view of this apparent difference in behaviour of the reactions of o-phenylenediamine with DBA and DMAD, we have reinvestigated the reaction of o-phenylenediamine with DBA with a view to ascertaining the structure of the addition product. Treatment of equimolar amounts of o-phenylenediamine and DBA in THF at room temperature gave a 80% yield of a product, identified as 2-(2-hydroxy-2-phenylethene)-3-phenylquinoxaline (22b). The structure of 22b has been established on the basis of analytical results and spectral data. The ir spectrum of this product, for example, did not show any carbonyl band. The nmr spectrum (Fig. III.5) of this product showed a sharp singlet at  $6.28\delta$  (1H) due to an olefinic proton and a broad signal at  $15.5\delta$  (1H) which was exchangeable with  $D_2O$  and is assigned to an enolic hydroxyl proton. In addition, the spectrum showed two multiplets centered around  $7.3\delta$  (10H) and  $7.6\delta$  (4H), assigned to the aromatic protons.

Further confirmation of the structure of 22b was derived from its  $^{13}C$ -nmr spectrum. The  $^{13}C$ -nmr spectrum (Fig. III.6) showed several signals at 94.1, 122.2, 128.6, 129.2, 131.1, 131.4, 131.8, 132.0, 132.3, 133.1, 133.5,

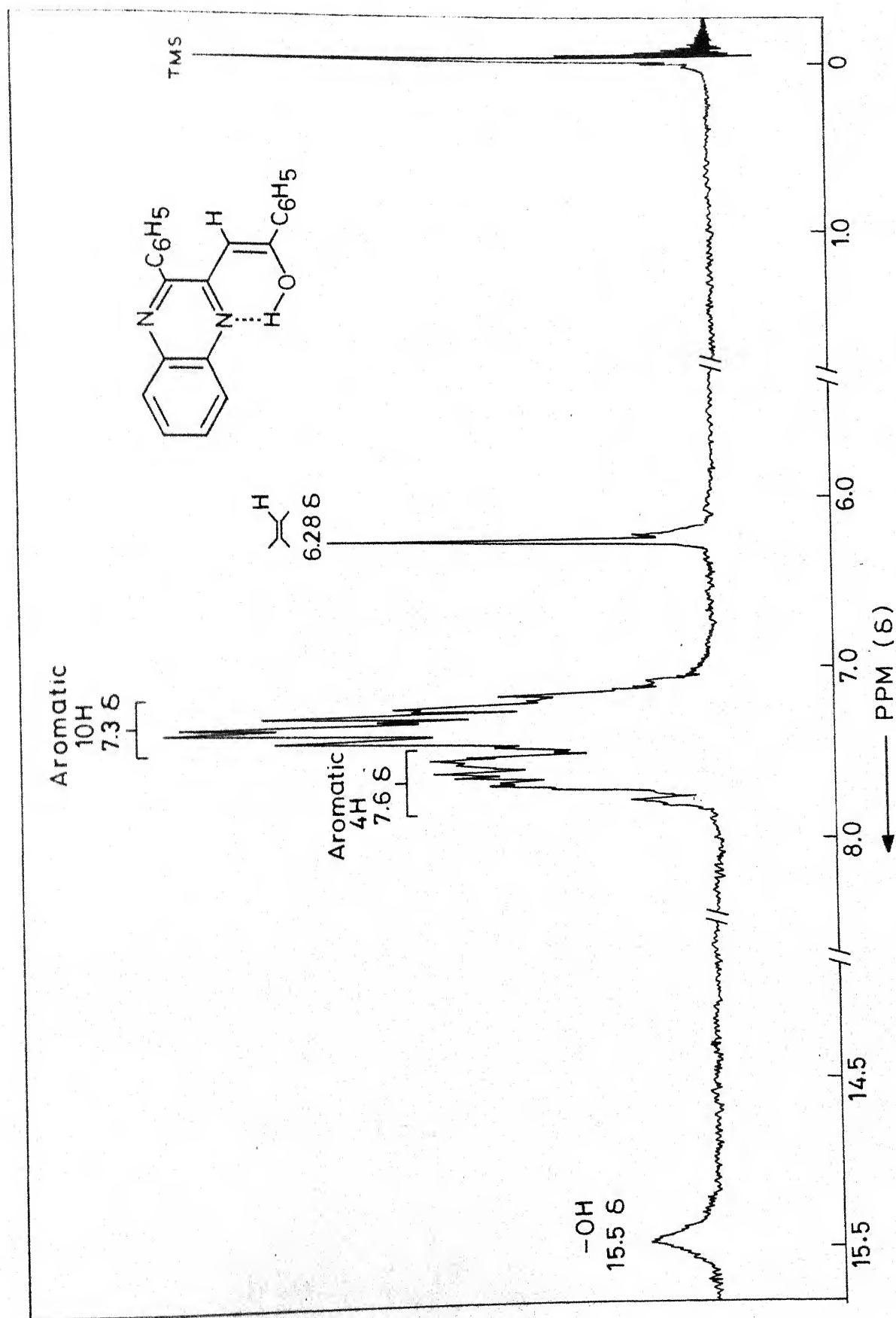


Fig. III.5 NMR spectrum (60 MHz) of 2-(2-hydroxy-2-phenyletheno)-3-phenylquinoxaline (22b)

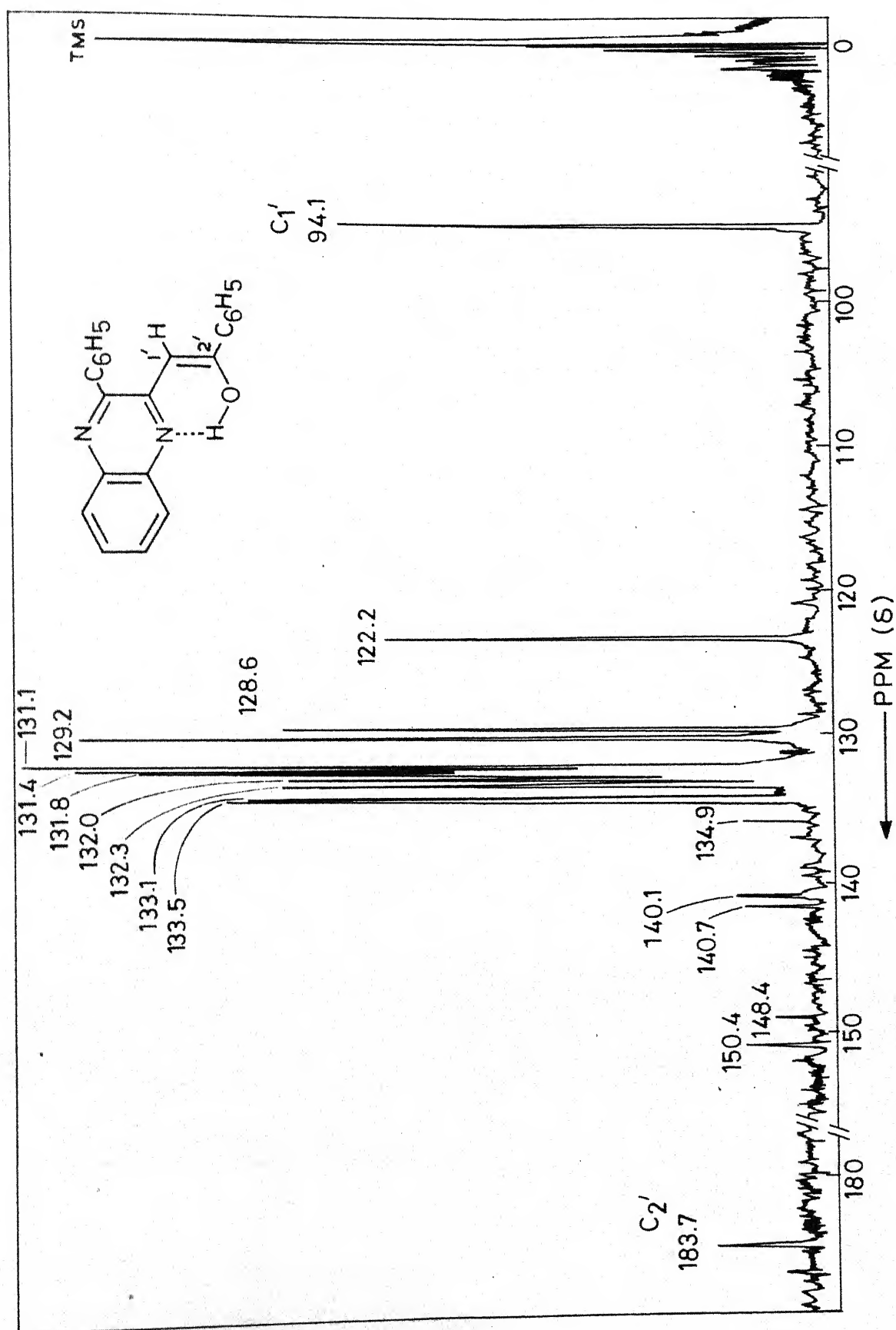


Fig.III.6  $^{13}\text{C}$ -NMR spectrum (25.2 MHz) of 2-(2-hydroxy-2-phenyletheno)-3-phenylquinoxaline (22b)

134.9, 140.1, 140.7, 148.4, 150.4 and 183.7  $\delta$ . Of these, the signal at 94.1  $\delta$  is assigned to the olefinic carbon ( $C_{1,}$ ), whereas, the signal at 183.7  $\delta$  is assigned to the  $sp^2$  carbon atom, bearing the enolic hydroxyl group ( $C_{2,}$ ). It might be mentioned in this connection that the  $^{13}C$ -nmr spectrum of dibenzoylmethane, which is known to exist in the enolic form, shows two signals at 92.5  $\delta$  and 184.9  $\delta$ , respectively, which are assigned to the olefinic carbon atom and the  $sp^2$  carbon atom to which the hydroxyl group is attached.<sup>36</sup>

The mass spectrum of 22b (Fig. III.7) showed the molecular ion peak at  $m/e$  324 (26). Other peaks were observed at  $m/e$  307 (20), 306 (3), 296 (24), 295 (6), 247 (11), 220 (20), 219 (46), 218 (14), 217 (3), 105 (100), 91 (6), 90 (3), 89 (6), 77 (49), 76 (11) and 51 (15). Some of the possible fragmentation modes are shown in Scheme III.9. The loss of an OH fragment from 22b, for example, will lead to the fragment 22c at  $m/e$  307, whereas, the fragment 22d at  $m/e$  306 could arise through the loss of  $H_2O$  from the molecular ion. A simple McLafferty rearrangement of 22b will result in the formation of 22a which can subsequently undergo fragmentation through different modes to give fragments like 22e, 22g, 22i and 22j at  $m/e$  296, 295, 247, 219 and 218, respectively. The highest intensity peak at  $m/e$  105 is assigned to the benzoyl fragment 22k (Scheme III.9).

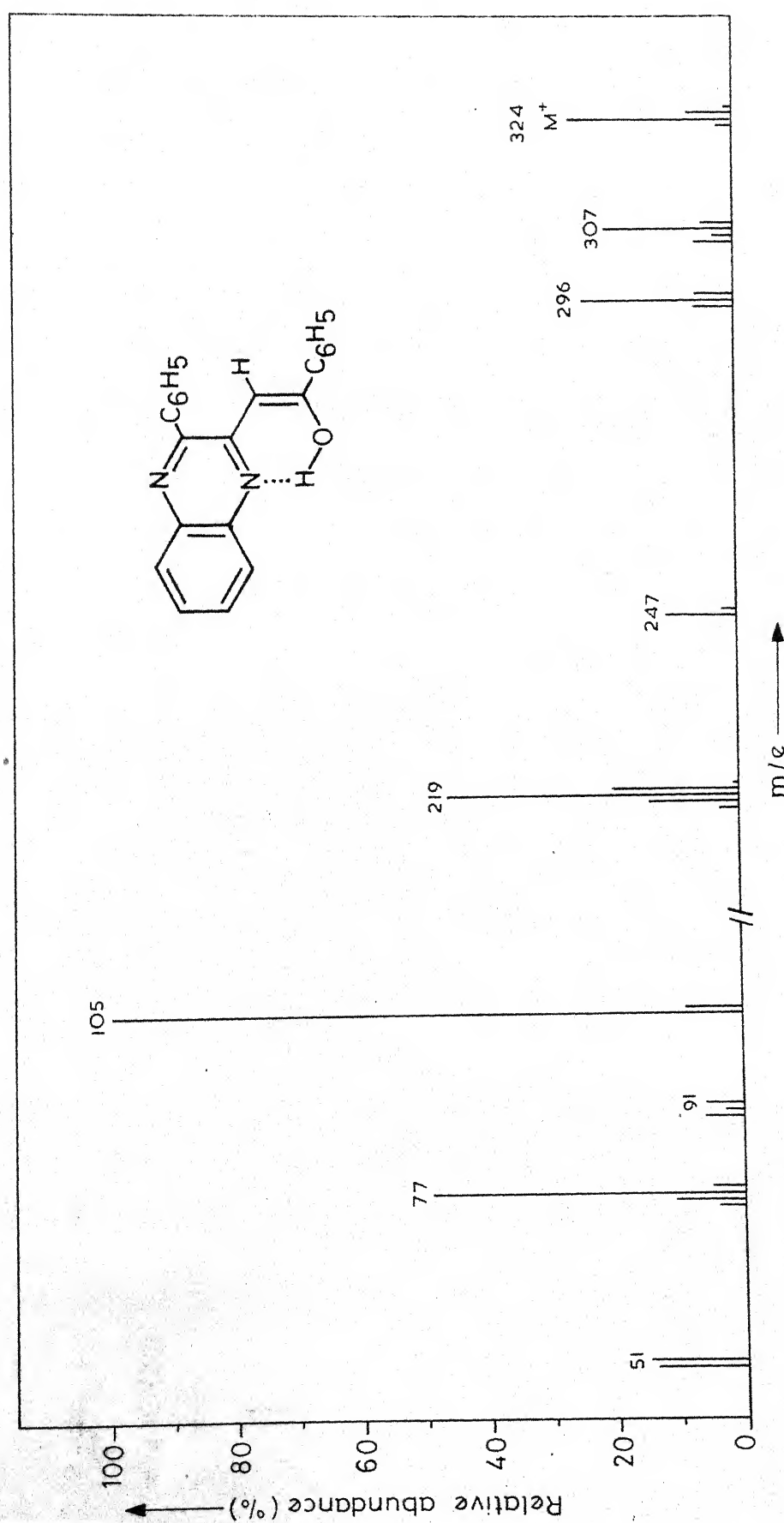


Fig.III.7 Mass spectrum of 2-(2-hydroxy-2-phenyletheno)-3-phenylquinoxaline (22b)







During the course of the present investigation, we came across a recent publication by Bass et.al.,<sup>37</sup> concerning the structure of the addition product, formed from the reaction of o-phenylenediamine with DBA. These authors have suggested that the structure of the product could be best represented by either 22a or 22b (Scheme III.8). In view of the uncertainty concerning the structure of the addition product, we have examined some of its chemical transformations for gaining further insight into this problem.

In an attempted bromination, the adduct 22, was treated with a solution of bromine in  $\text{CCl}_4$  which resulted in the formation of a 98% yield of a product identified as 2-bromophenacyl-3-phenylquinoxaline (23) (Scheme III.10). Analytical results have shown that the compound has the molecular formula  $\text{C}_{22}\text{H}_{15}\text{N}_2\text{OBr}$ . The ir spectrum of 23 showed an intense peak at  $1710\text{ cm}^{-1}$  due to carbonyl group absorption. The nmr spectrum of the bromo adduct 23 (Fig. III.8) showed a sharp singlet at  $6.75\delta$  (1H) due to a methine proton, attached to strongly electron-withdrawing groups. In addition, the spectrum showed two multiplets centred around  $7.62\delta$  (12H) and  $8.06\delta$  (2H), which could be assigned to the aromatic protons.

The uv spectrum of 23 (Fig. III.9) showed two absorption maxima at 247 nm ( $\epsilon$ , 29,500) and 332 nm ( $\epsilon$ , 6,300). It

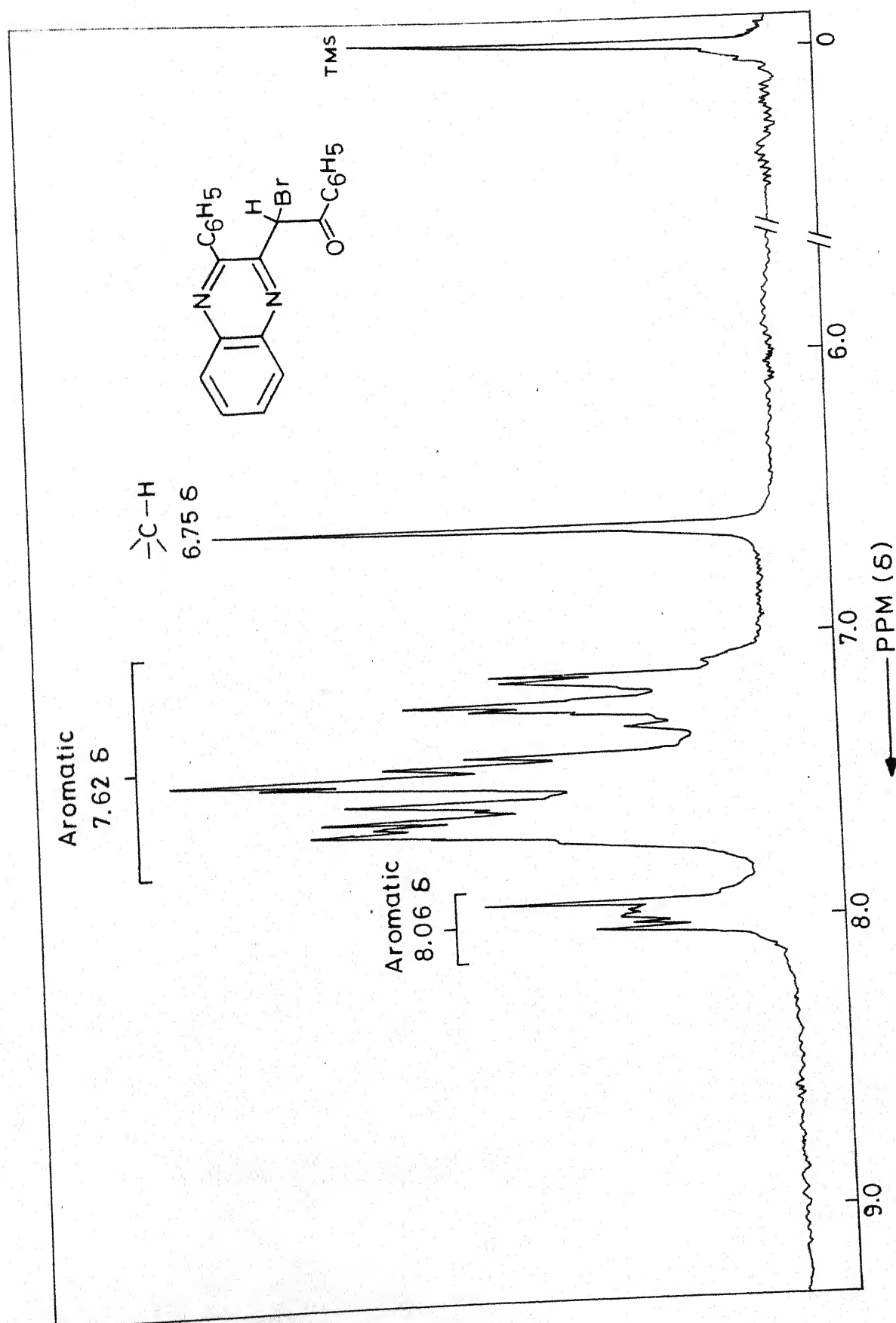


Fig.III.8 NMR spectrum(100MHz) of 2-bromophenacyl-3-phenylquinoxaline (23)

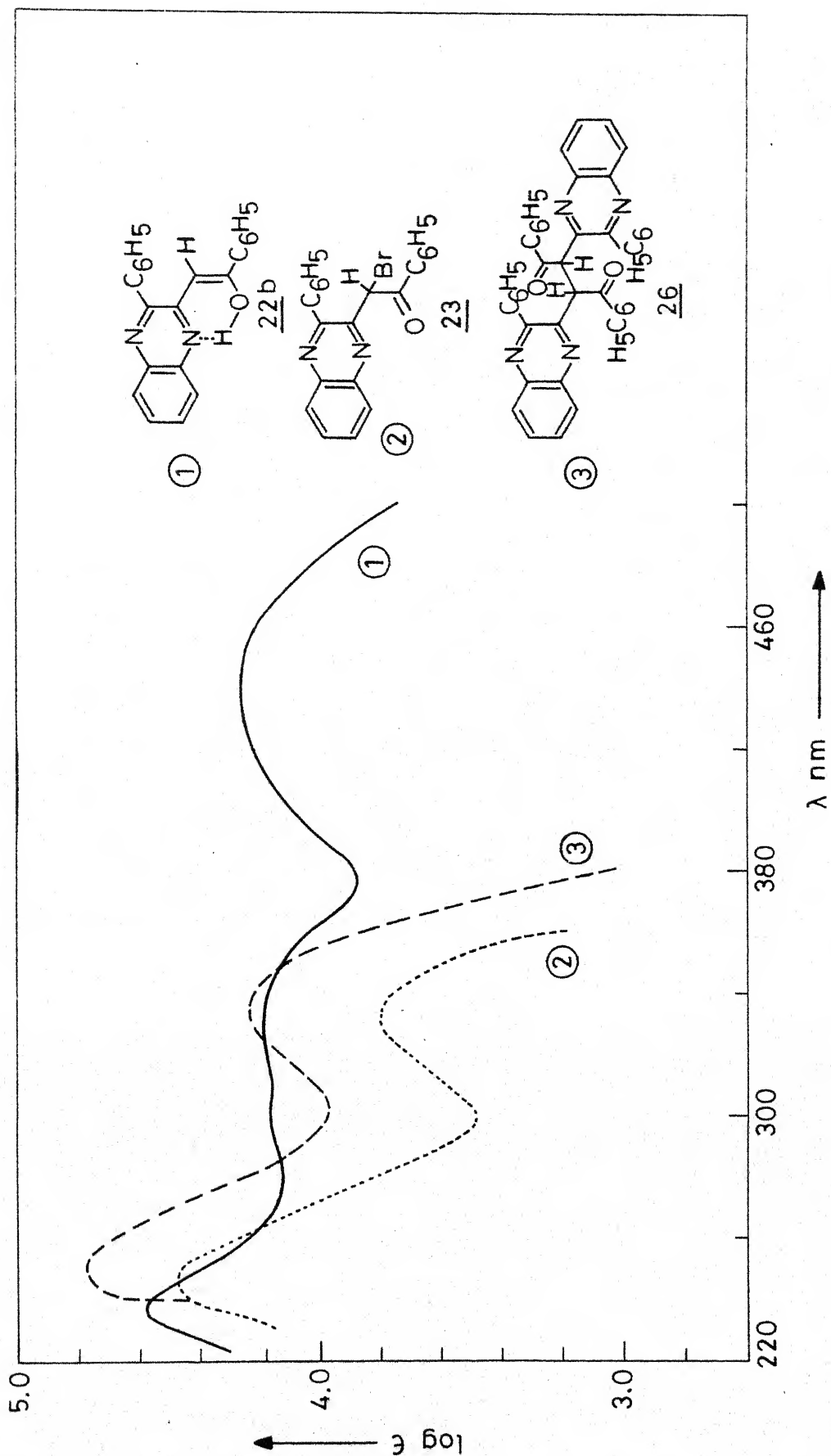


Fig. III.9 Electronic spectra of 22b, 23 and 26

is known that the quinoxaline chromophore exhibits an  $n \rightarrow \pi^*$  band around 312 nm and that a bathochromic shift of this band is observed with substitution in the 2-position of the quinoxaline ring.<sup>38</sup> The presence of the long wavelength absorption band at 332 nm in the uv spectrum of 23 would be in support of the assigned structure. Examination of Fig. III.9 reveals that the uv spectrum of the bromo derivative, 23, is considerably different from that of the starting material, 22b, as would be expected from their structural variations.

Further confirmation of the structure of 23 was derived from its  $^{13}\text{C}$ -nmr spectrum. The  $^{13}\text{C}$ -nmr spectrum of 23 (Fig. III.10) showed several signals at 55.6, 131.3, 131.8, 132.1, 132.5, 133.3, 134.1, 136.1, 140.3, 144.2 and 152.6  $\delta$ . Of these, the signals at 55.6  $\delta$  is assigned to the  $\text{sp}^3$  carbon atom, bearing the bromine atom and the other electron-withdrawing functional groups.

Additional support for the structure of 23 was derived from its mass spectrum (Fig. III.11). The mass spectrum showed a molecular ion peak at  $m/e$  402(3). Other peaks in the spectrum were observed at  $m/e$  325(5), 324 (26), 323 (54), 322 (12), 321 (3), 297 (2), 296 (7), 295 (7), 294 (4), 218 (12), 105 (100), 77 (71) and 51 (3), which could be assigned to some of the fragments shown in Scheme III.11. Loss of a bromine atom from the molecular

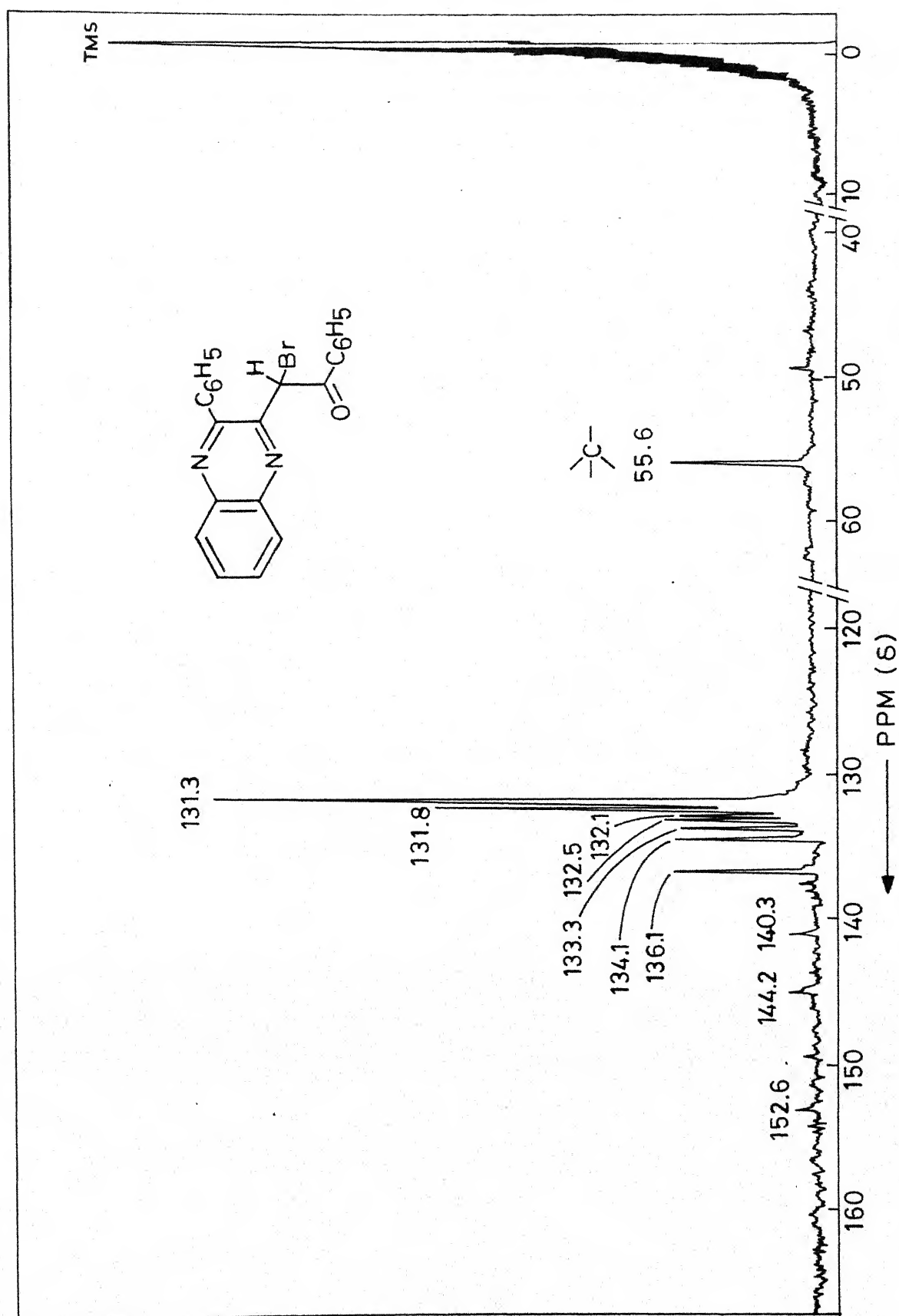


Fig. III.10 <sup>13</sup>C-NMR spectrum (25.2 MHz) of 2-bromophenacyl-3-phenylquinoxaline (23)

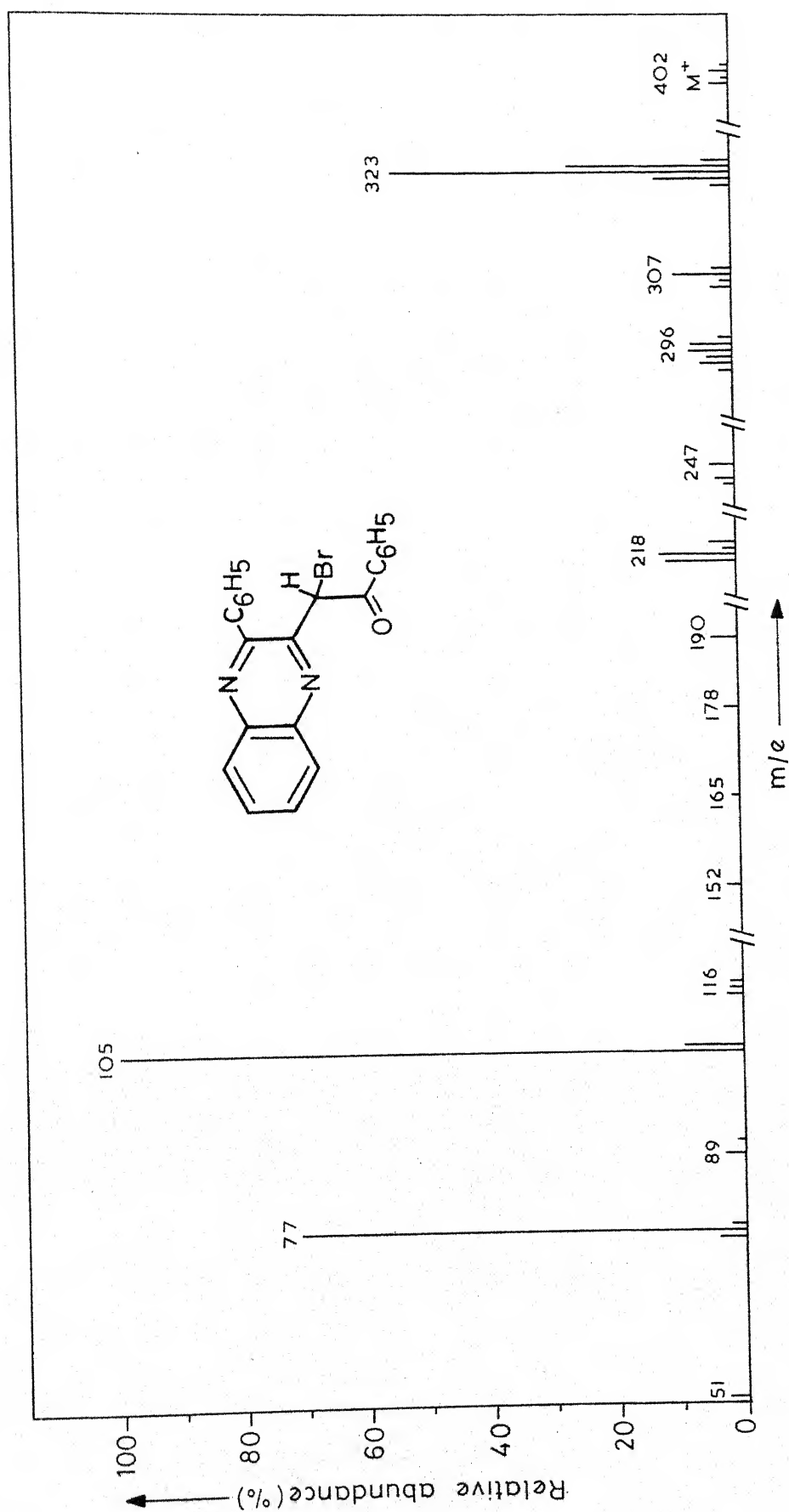
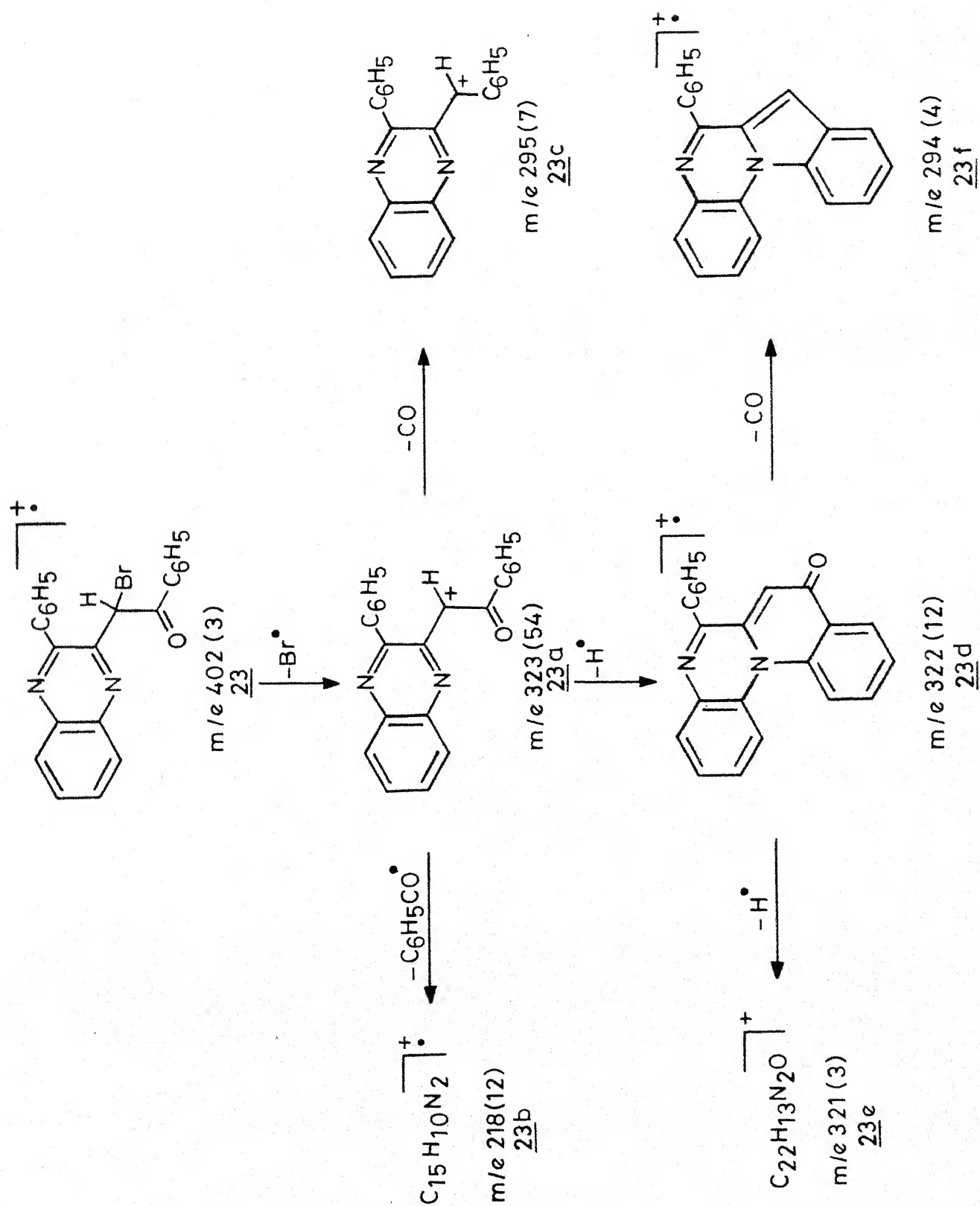


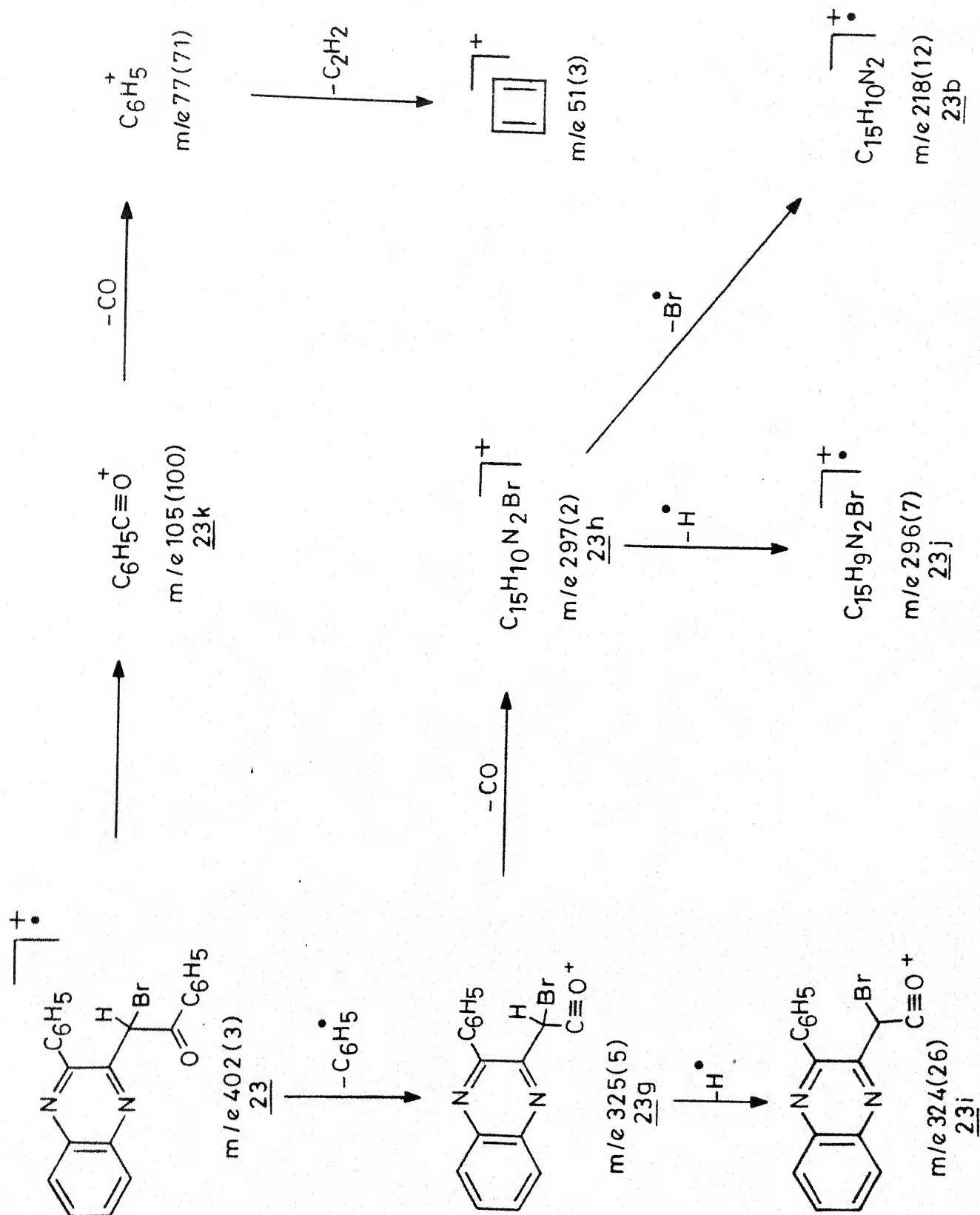
Fig. III.11 Mass spectrum of 2-bromophenacyl-3-phenylquinoxaline (23)



Scheme III.11



Scheme III.11 (contd)



ion will give the fragment 23a at m/e 323, which in turn can lose fragments like  $C_6H_5CO$ , CO and H, to give peaks at m/e 218 (23b), 295 (23c) and 322 (23d), respectively. The fragment 23d can subsequently lose a hydrogen atom to give the fragment 23e at m/e 321, whereas the loss of a CO group will lead to the formation of 23f at m/e 294. On the other hand, the loss of a phenyl group from the molecular ion will result in the fragment 23g at m/e 325, which can subsequently lose a hydrogen atom to give the fragment 23i at m/e 324. Loss of a CO group from 23g can lead to the fragment 23h at m/e 297. The highest intensity peak at m/e 105 is assigned to the benzoyl fragment 23k, formed from the molecular ion peak.

Further support for the structure 22b for the addition product of o-phenylenediamine and DBA is derived from its oxidation studies. Treatment of 22 with a nonstoichiometric oxide like nickel peroxide in benzene, resulted in the formation of 38% yield of an oxidative dimer having the molecular formula  $C_{44}H_{30}N_4O_2$  and identified as 1,4-diphenyl-2,3-bis(3-phenylquinox-2-yl)-1,4-butanedione (26) (Scheme III.12). The mass spectrum of 26 showed a molecular ion peak at m/e 646. The ir spectrum of this product showed a carbonyl absorption band at  $1676\text{ cm}^{-1}$ . The uv spectrum of 26 showed two absorption maxima at 252 nm ( $\epsilon$ , 60,000) and 336 nm ( $\epsilon$ , 17,000), respectively,

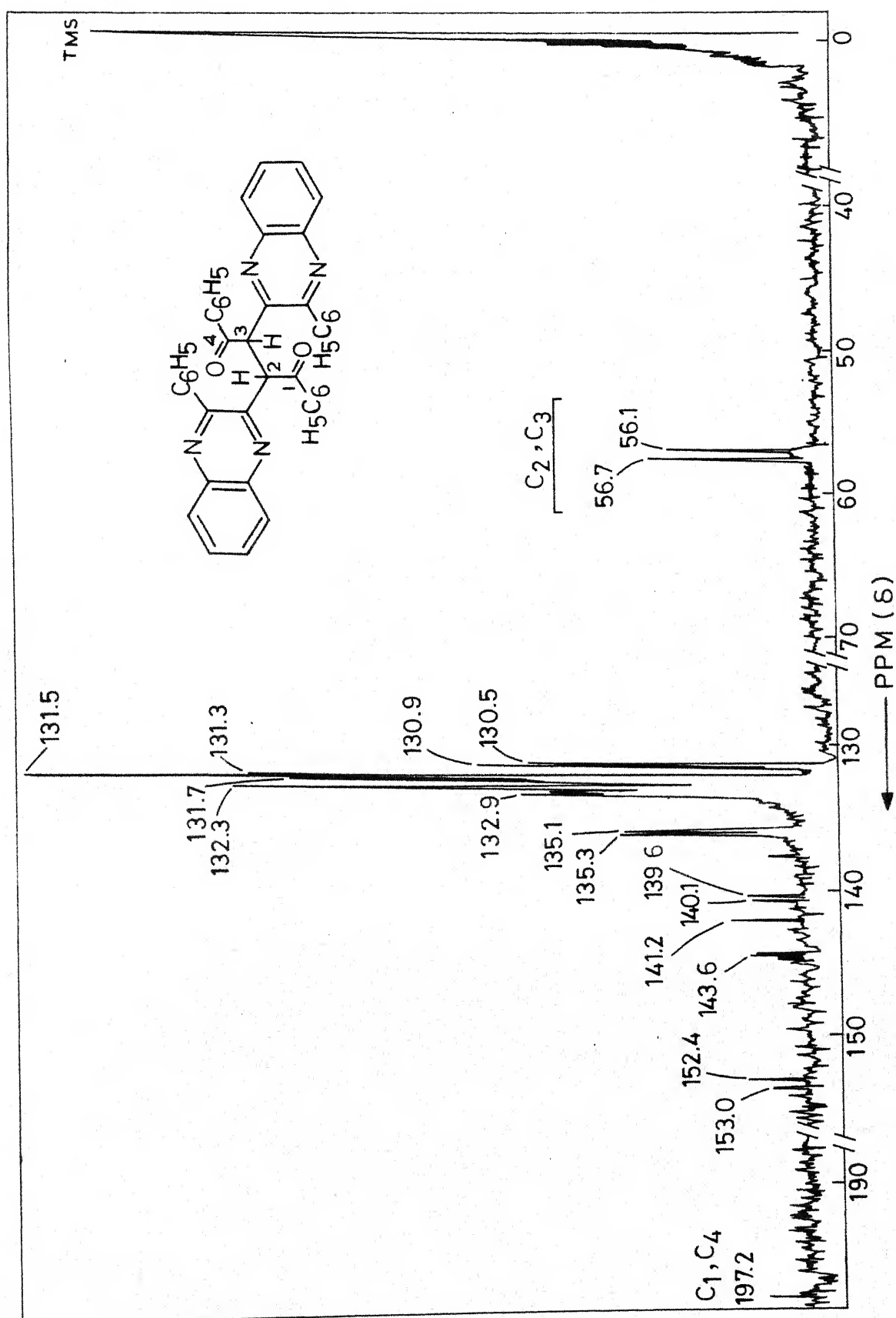


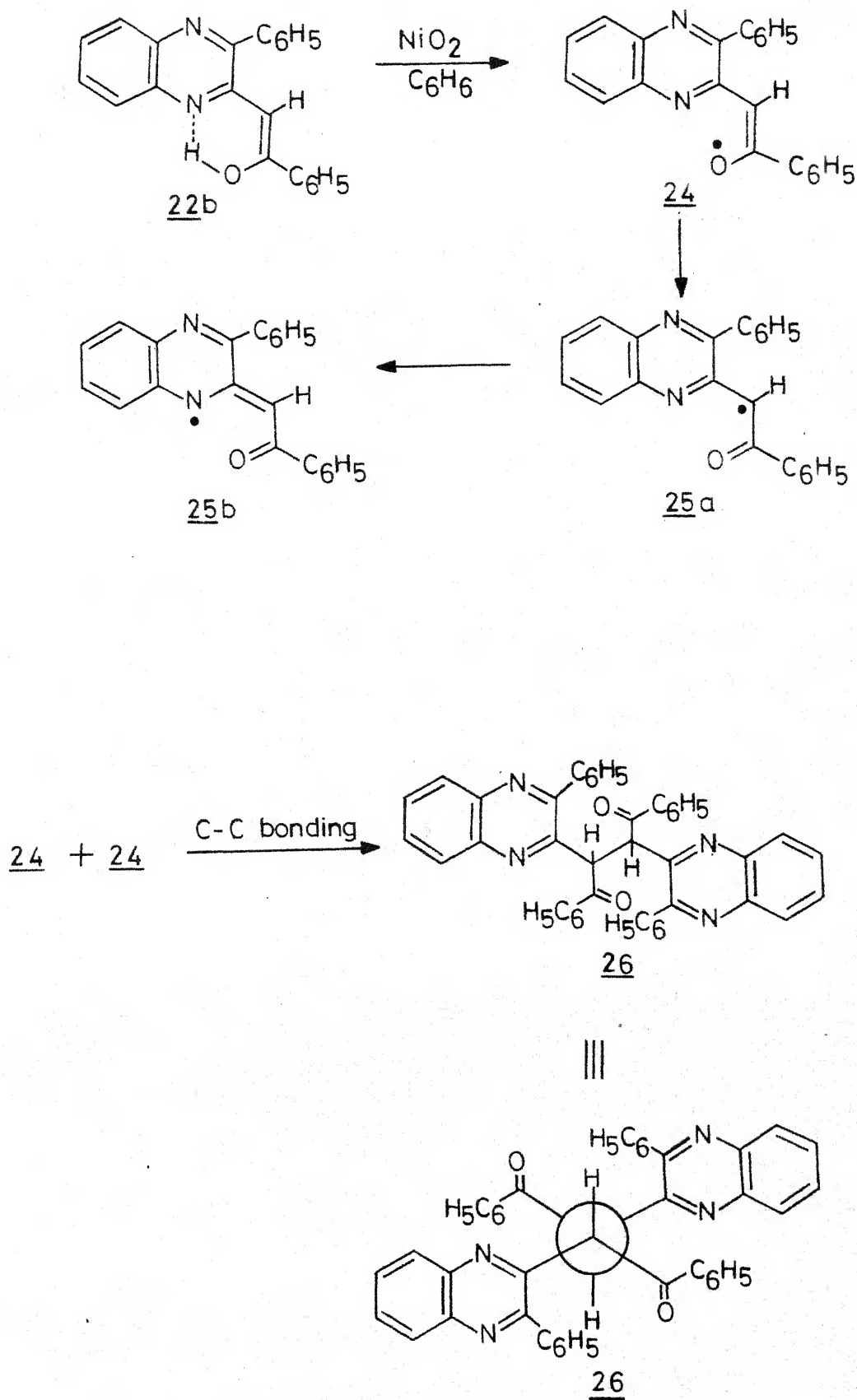
Fig.III.12  $^{13}\text{C}$ -NMR spectrum (25.2 MHz) of 1,4-diphenyl -2,3-bis(3-phenylquinox-2-yl)-1,4-butane-dione (36)

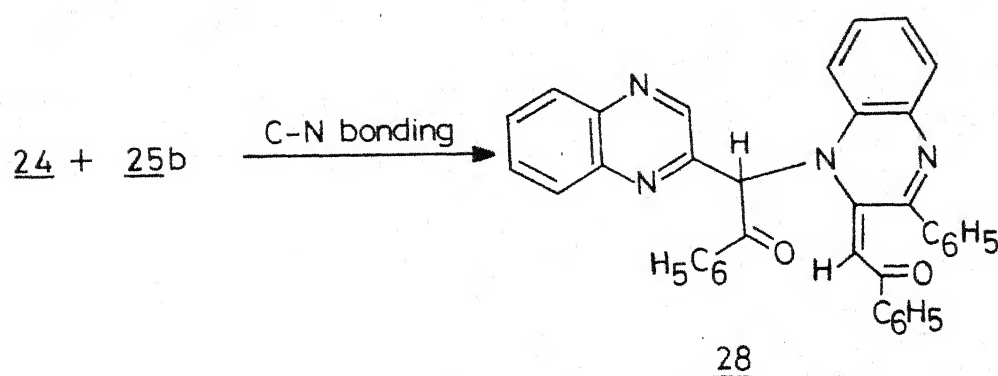
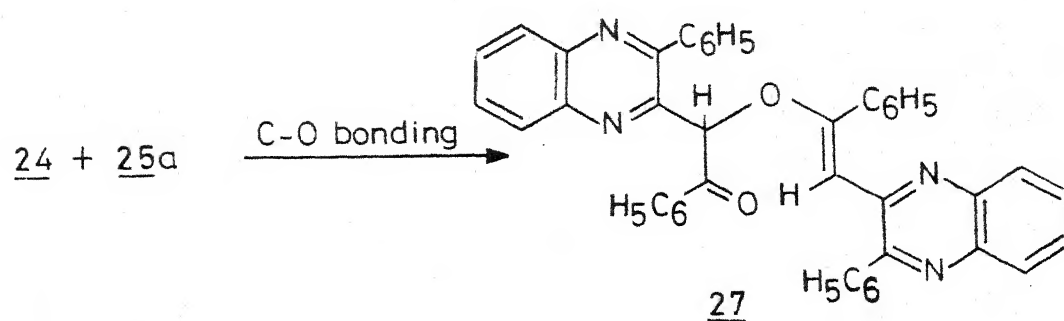
and was found to be very similar to the spectrum of the bromo derivative 23 (Fig. III.9), indicating the presence of a similar chromophore in 26.

The proton nmr spectrum of 26 showed a series of signals in the region of 6.95 $\delta$  - 8.10 $\delta$ , due to the aromatic and methine protons. The  $^{13}\text{C}$ -nmr spectrum of 26 (Fig. III.12) showed several signals at 56.1, 56.7, 130.5, 130.9, 131.3, 131.5, 131.7, 132.3, 132.9, 135.1, 135.3, 139.6, 140.1, 141.2, 143.6, 152.4, 153.0 and 197.2  $\delta$ . Of these, the signals at 56.1 $\delta$  and 56.7 $\delta$  could be assigned to the two  $\text{sp}^3$  carbon atoms present in 26. However, the exact reason for the slight magnetic non-equivalence of these two carbon atoms is not very clear at present. The signal at 197.2 $\delta$  is assigned to the  $\text{sp}^2$  carbon atoms of the two carbonyl groups present in 26.

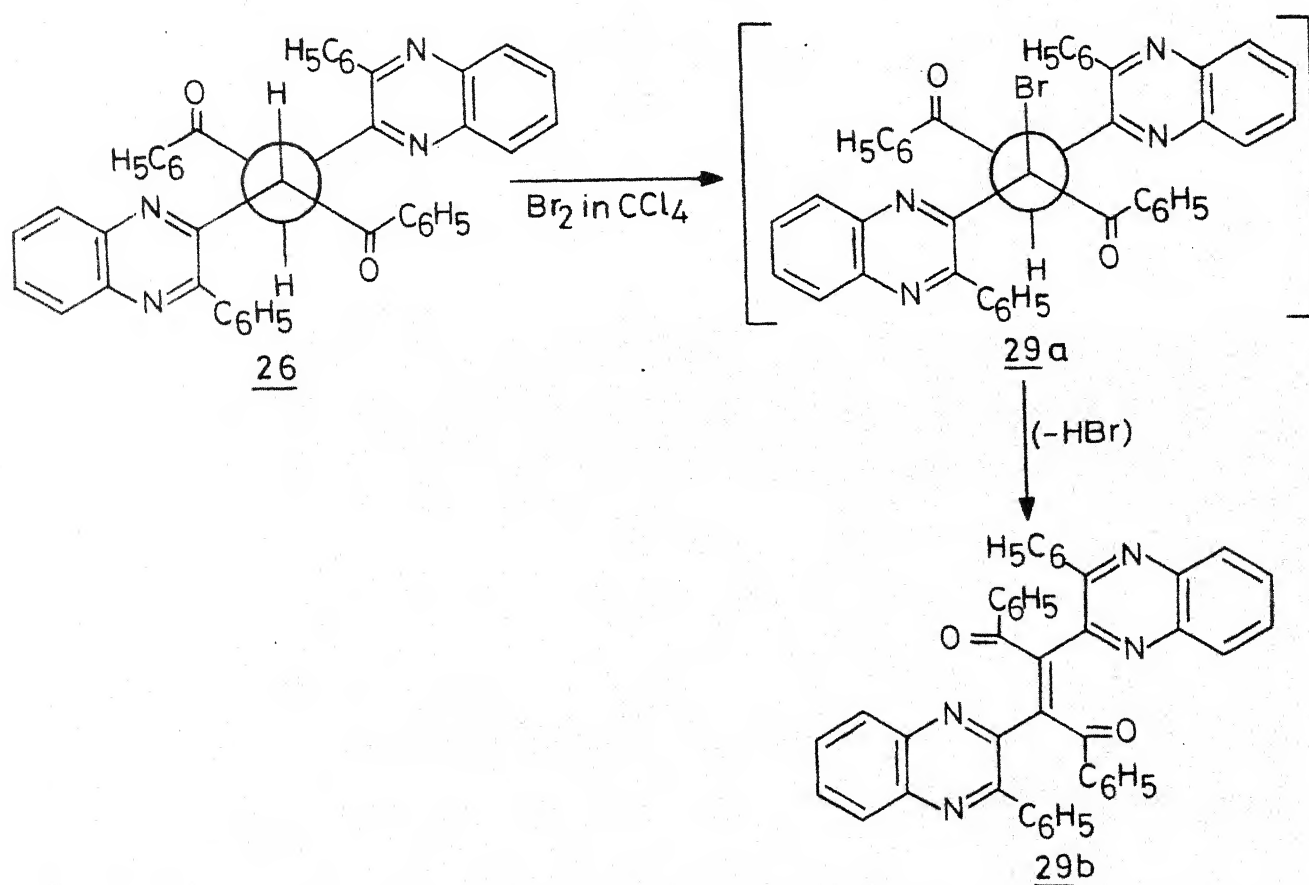
A probable mechanism for the formation of the oxidative dimer 26 is shown in Scheme III.12. Treatment of the quinoxaline derivative 22b with nickel peroxide will lead to the formation of the radical intermediate 24, which can subsequently be isomerized to other radical intermediates like 25a and 25b. Of the several possible radical recombination modes, the ones involving a C-C linkage, C-O linkage and C-N linkage and leading to the dimers 26, 27 and 28, respectively are shown in Scheme III.12. Of these possibilities, it appears that the C-C bond forming mode of

## Scheme III. 12





## Scheme III. 13





radical recombination, involving the dimerization of the radical intermediate 24 and leading to the formation of 26 is the most favoured pathway.

Additional support for the structure 26 for the oxidative dimer is derived from its attempted bromination.<sup>39</sup> Treatment of 26 with bromine in carbon tetrachloride resulted in the formation of a 82% yield of a product having the molecular formula  $C_{44}H_{28}N_4O_2$  and identified as 1,4-diphenyl-2,3-bis(3-phenylquinox-2-yl)-2-butene-1,4-dione (29b). The structure of 29b was derived from analytical data and spectral evidences. The mass spectrum of 29b, for example, showed the molecular ion peak at  $m/e$  644. The uv spectrum of 29b showed absorption maxima at 250 nm ( $\epsilon$ , 65,000) and 356 nm ( $\epsilon$ , 21,000) and was different from the spectra of both 22b and 26 (Fig. III.13). It might be mentioned here that the structure of 29b is assumed to have the trans-geometry, on the basis of steric considerations, although we have no definitive evidences in support of this assignment. The formation of 29b from the dimer 26 can be rationalized in terms of the initial formation of the monobromo derivative, 29a, which can lose HBr during the course of the reaction to give the product (Scheme III.13).

In continuation of our studies, we have examined the reaction of 1,8-diaminonaphthalene with DBA with a

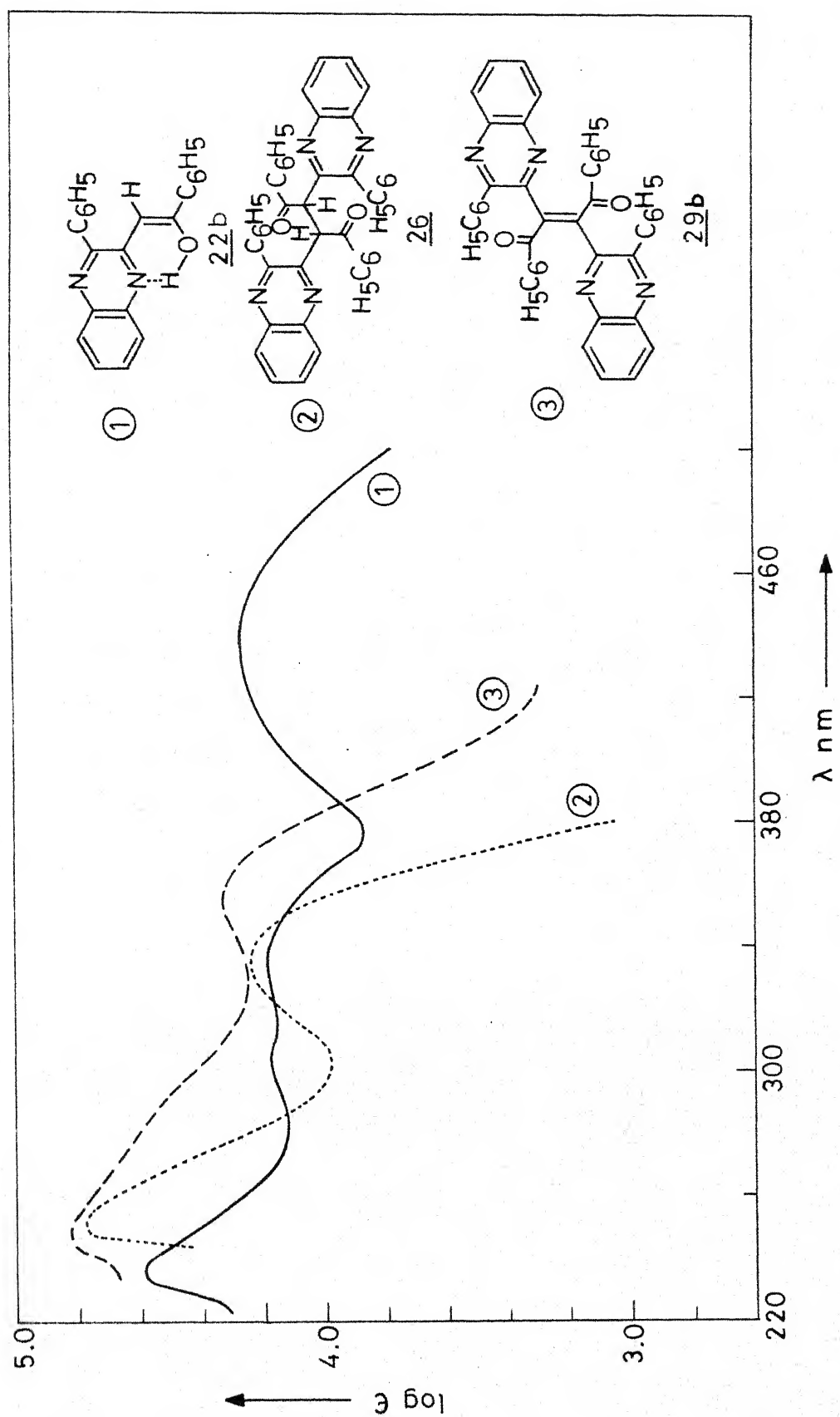
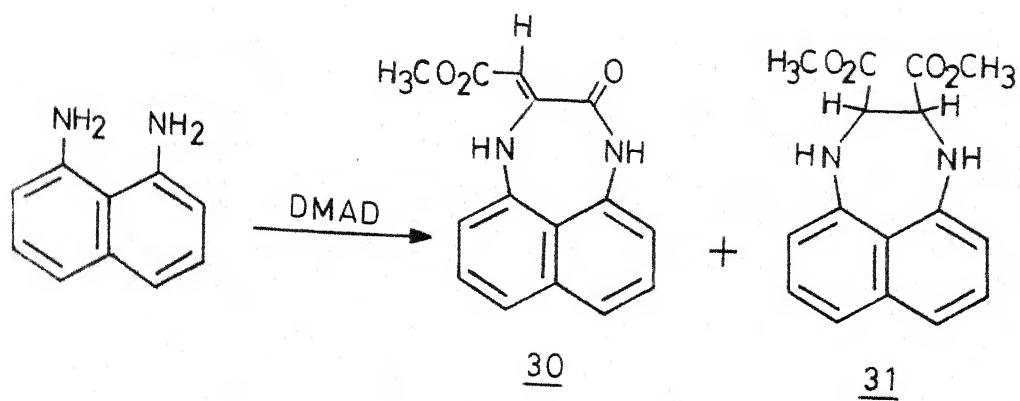


Fig. III.13 Electronic spectra of 22b, 26 and 29b

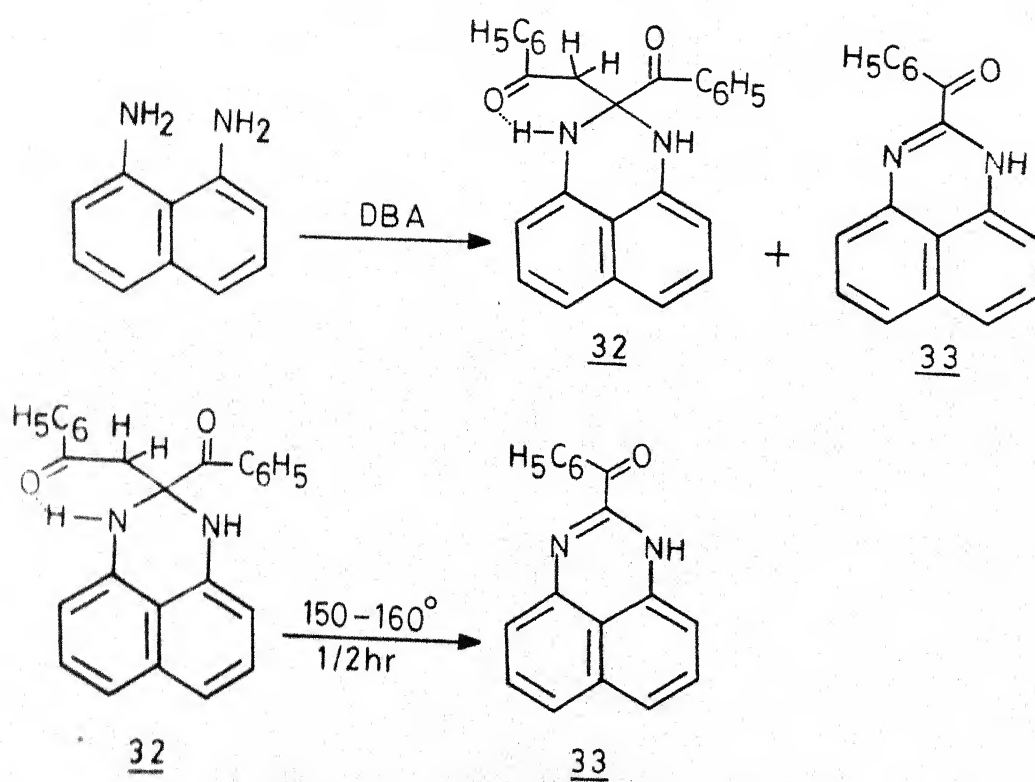
view to studying the nature of the products formed in this case. The reaction of 1,8-diaminonaphthalene with dimethyl acetylenedicarboxylate is reported to give a mixture of products consisting of 2-oxo-2-carbomethoxymethylene-1,2,3,4-tetrahydronaphtho-[1,8-ef]-[1,4]-diazepin (30) and 2,3-dicarbomethoxy-1,2,3,4-tetrahydronaphtho-[1,8-ef]-[1,4]-diazepin (31) (Scheme III.14).<sup>40</sup> Treatment of an equimolar mixture of 1,8-diaminonaphthalene and DBA in THF at room temperature gave a mixture of products consisting of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine (32) (9%) and 2-benzoylperimidine (33) (89%) (Scheme III.15). The structures of both 32 and 33 have been arrived at on the basis of analytical results and spectral information.

Compound 33, for example, analyzed for  $C_{18}H_{12}N_2O$ . Its ir spectrum showed an NH stretching frequency at  $3360\text{ cm}^{-1}$  and a carbonyl band at  $1658\text{ cm}^{-1}$ , respectively. In addition, the spectrum showed absorption bands at 1624, 1599 and  $1520\text{ cm}^{-1}$ , characteristic of the stretching frequencies of 2-substituted perimidine systems.<sup>41</sup> The proton nmr spectrum of 33 (Fig. III.14) showed a multiplet at  $\delta$  9.38 (1H) assigned to the  $H_9$ -proton of the perimidine nucleus. The upfield shift of this proton is attributed to the presence of the adjacent NH group of the perimidine ring. Other protons of the perimidine ring appeared as a complex multiplet centred around 7.55 $\delta$  (3H) and 8.31 $\delta$  (2H

Scheme III.14



Scheme III.15



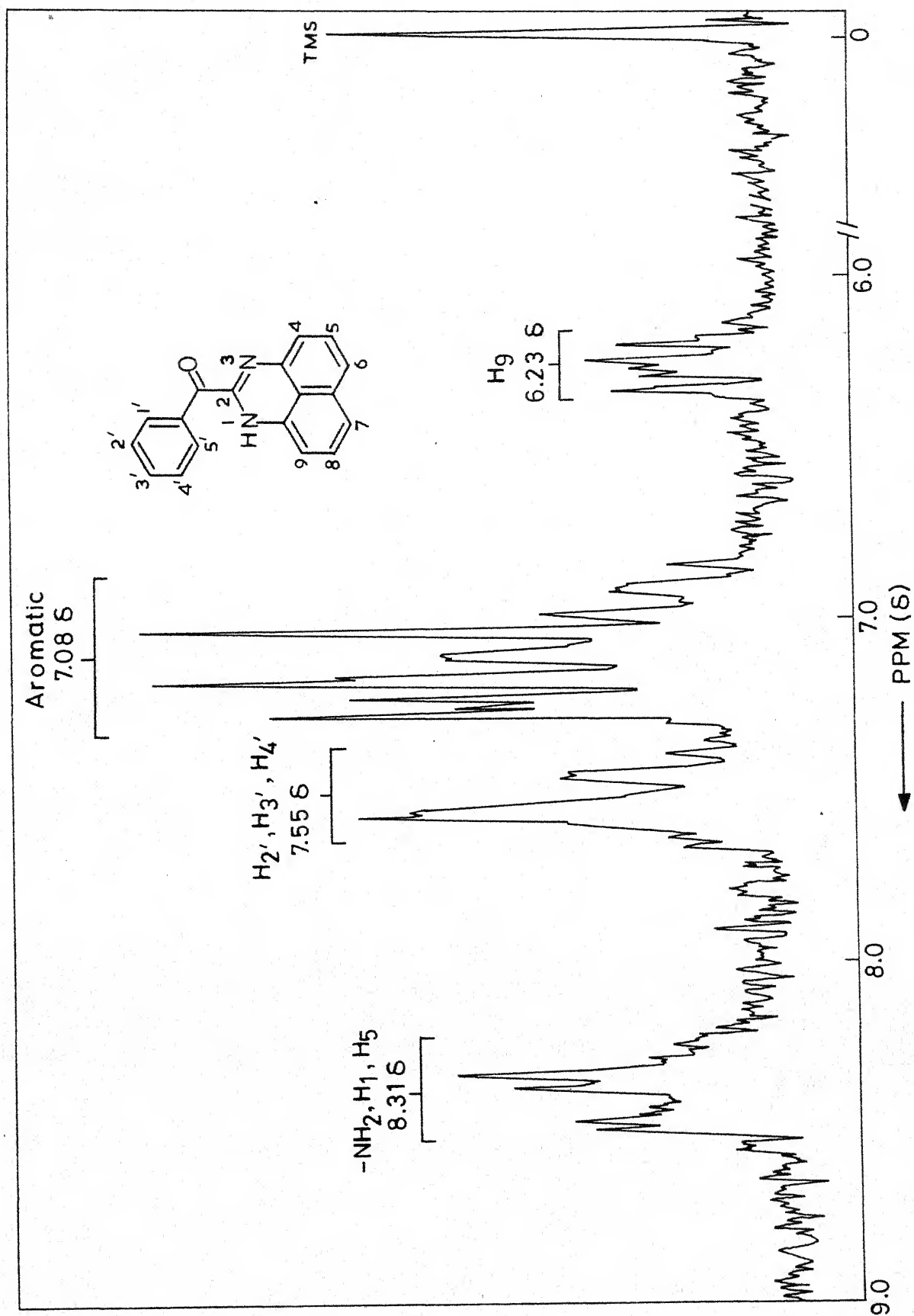


Fig. III.14 NMR spectrum (60 MHz) of 2-benzoylperimidine (33)

and NH), respectively. The multiplet at 8.31 $\delta$  accounted for three protons, which include the NH proton of the perimidine ring system.

The mass spectrum of 33 (Fig. III.15) showed a molecular ion peak at m/e 272 (100). Other peaks in the spectrum were observed at m/e 271 (14), 244 (12), 243 (3), 105 (41), 77 (71) and 51 (6). Some of the possible fragmentation modes are shown in Scheme III.16.

Analytical results have shown that compound 32 has the molecular formula  $C_{26}H_{20}N_2O_2$ . The ir spectrum of 32 showed a band at 3276  $cm^{-1}$ , characteristic of a hydrogen-bonded NH group. In addition, the spectrum showed a CO absorption band at 1650  $cm^{-1}$ . The proton nmr spectrum of 32 (Fig. III.16) showed an AB quartet with chemical shifts at 3.14 $\delta$  (1H) and 4.53 $\delta$  (1H) and  $J_{AB} = 17.5$  cps, indicating the presence of two non-equivalent methylene protons.<sup>42</sup> The magnetic nonequivalence of the two methylene protons may be attributed to the restricted rotation of the  $C_6H_5COCH_2$  group due to the hydrogen-bonding between the NH and CO groups in 32.<sup>43</sup> In addition, the spectrum of 32 showed several multiplets centred around 6.07 $\delta$  (2H), 6.5 $\delta$  (1H), 7.0 $\delta$  (5H), 7.48 $\delta$  (6H) and 7.92 $\delta$  (4H). Of these, the multiplets at 7.48 $\delta$  and 7.92 $\delta$  are assigned to the benzoyl group protons, whereas, the other multiplets at 6.07 $\delta$ , 6.5 $\delta$  and 7.0 $\delta$  account for the aromatic protons of the perimidine nucleus and the two NH protons.

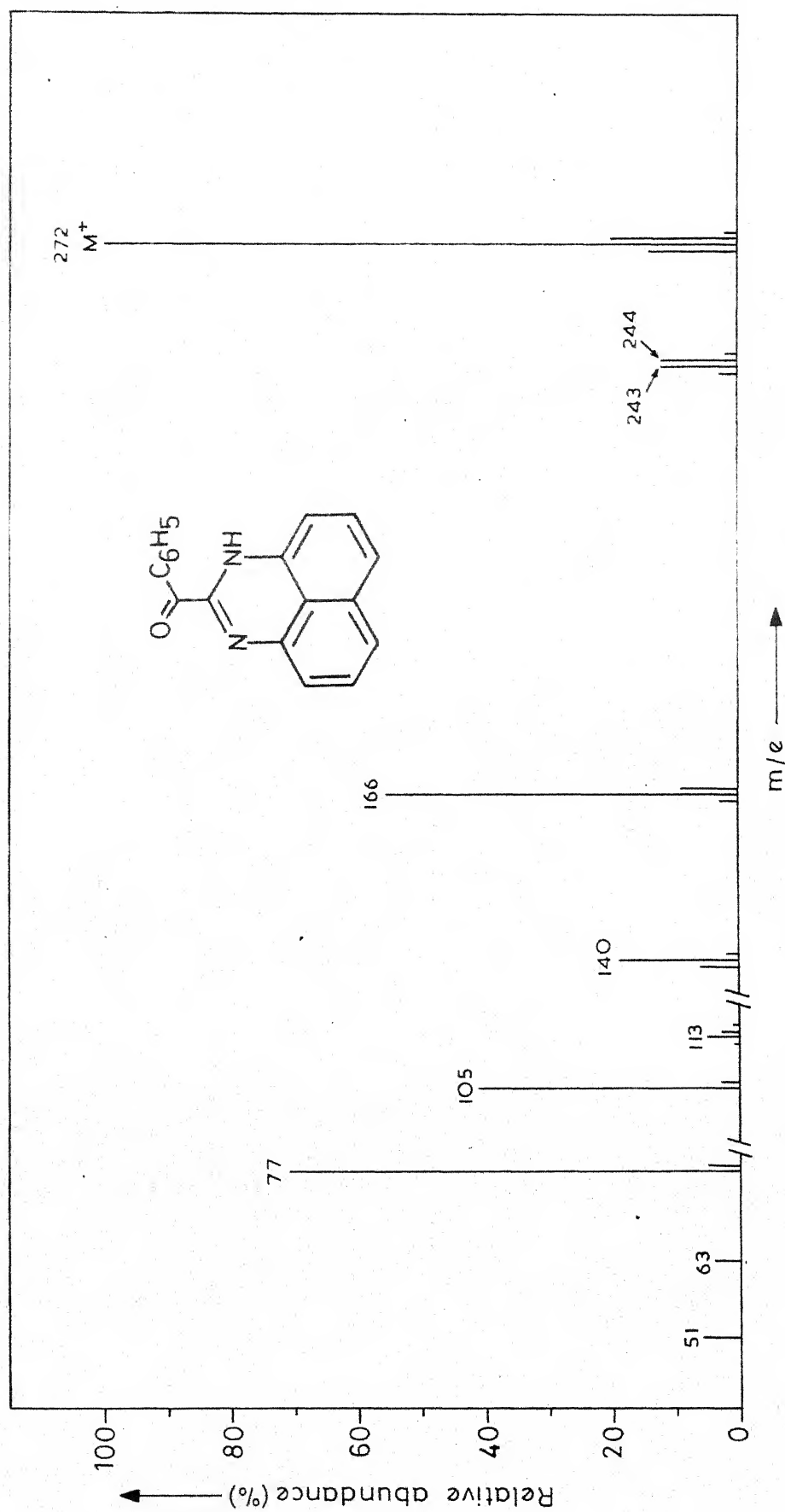
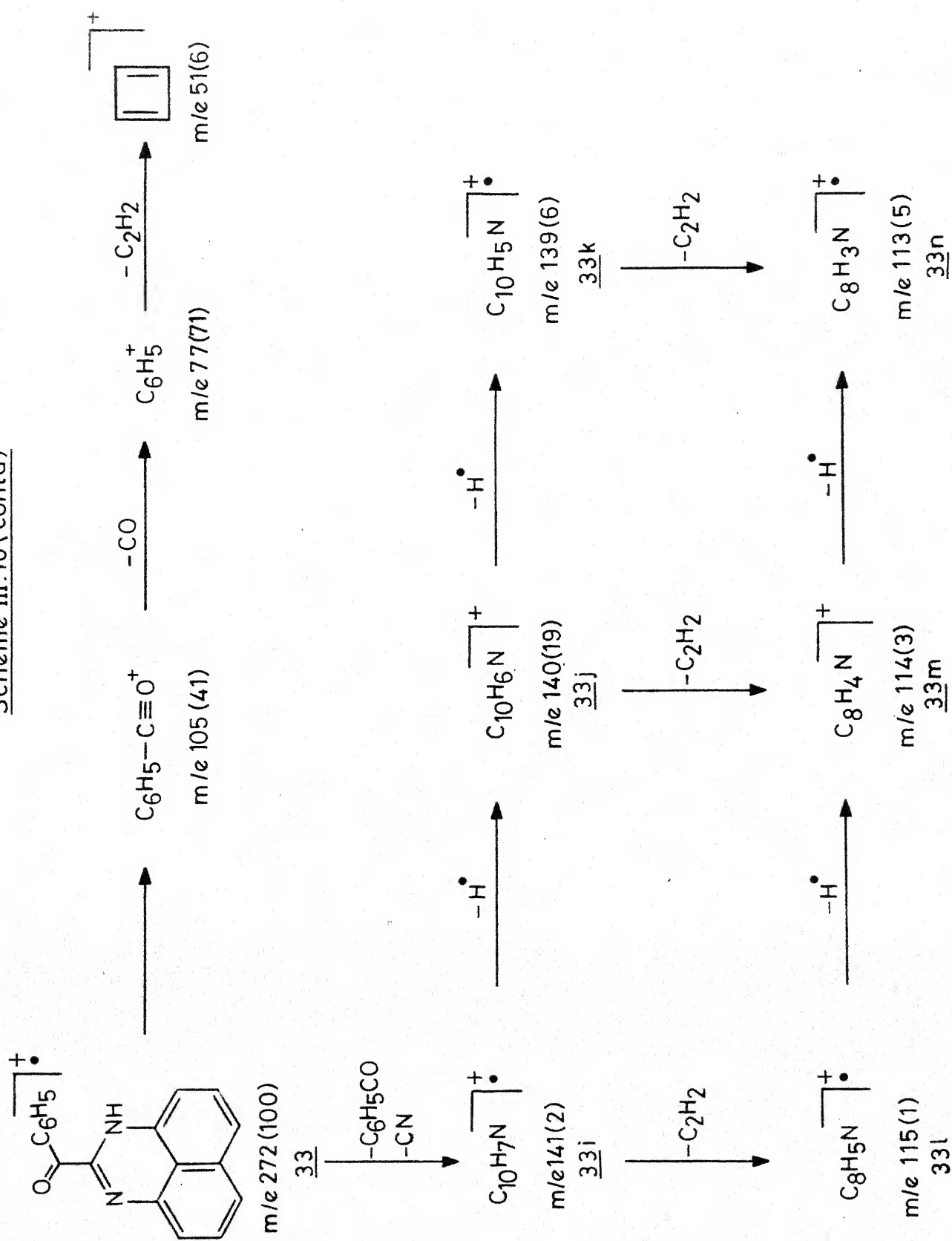


Fig. III.15 Mass spectrum of 2-benzoylperimidine (33)





Scheme III.16 (contd)



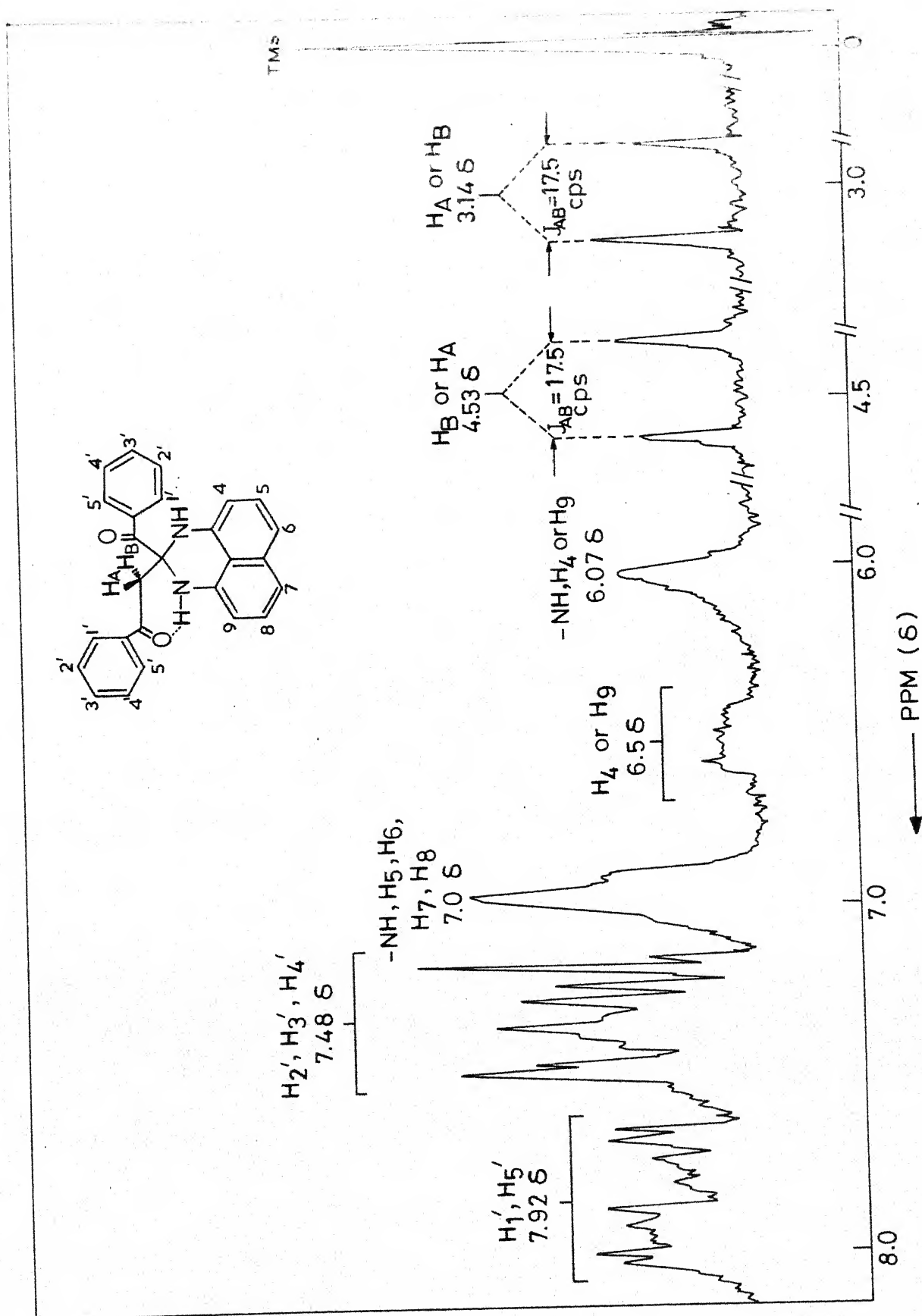


Fig.III.16 NMR spectrum(60 MHz) of 2-benzoyl-2,3-dihydroperimidine (32)

Further support for the structure of 32 was derived from its mass spectrum. The mass spectrum of 32 (Fig. III.17) showed a molecular ion peak at m/e 392 (4). Other peaks in the spectrum were observed at m/e 375 (1), 374 (3), 272 (61), 271 (7), 270 (2), 269 (2), 268 (1), 244 (7), 243 (7), 242 (7), 166 (30), 141 (2), 140 (11), 139 (4), 105 (100), 77 (98) and 51 (40), which could be assigned to some of the fragments shown in Scheme III.17. As is evident from Scheme III.17, a prominent mode of fragmentation of 32 is through the loss of a  $C_6H_5COCH_3$  moiety to give the molecular ion of 33 at m/e 272. The peaks at m/e 271, 244, 243, 242, 166, 141, 140 and 139 can be assigned to fragments like 33a, 33b, 33c, 33e, 33f, 33i, 33h and 33k, formed through the fragmentation of the molecular ion of 33 (see, Fig. III.15 and Scheme III.16). The mass spectrum of 32 clearly reveals that compound 32 is very readily transformed to 33, under electron impact. Other peaks in the mass spectrum of 32 at m/e 375, 374, 269 and 268 could be assigned to the fragments 32a, 32b, 32c and 32d, as shown in Scheme III.17.

Additional support for the structure of 32 was derived from its thermal decomposition studies. On heating 32 around 150-160° for 1/2 hr resulted in the formation of a 73% yield of 33. The formation of 33 from 32 is rationalized in terms of a concerted loss of an aceto-phenone fragment as shown in Scheme III.15.

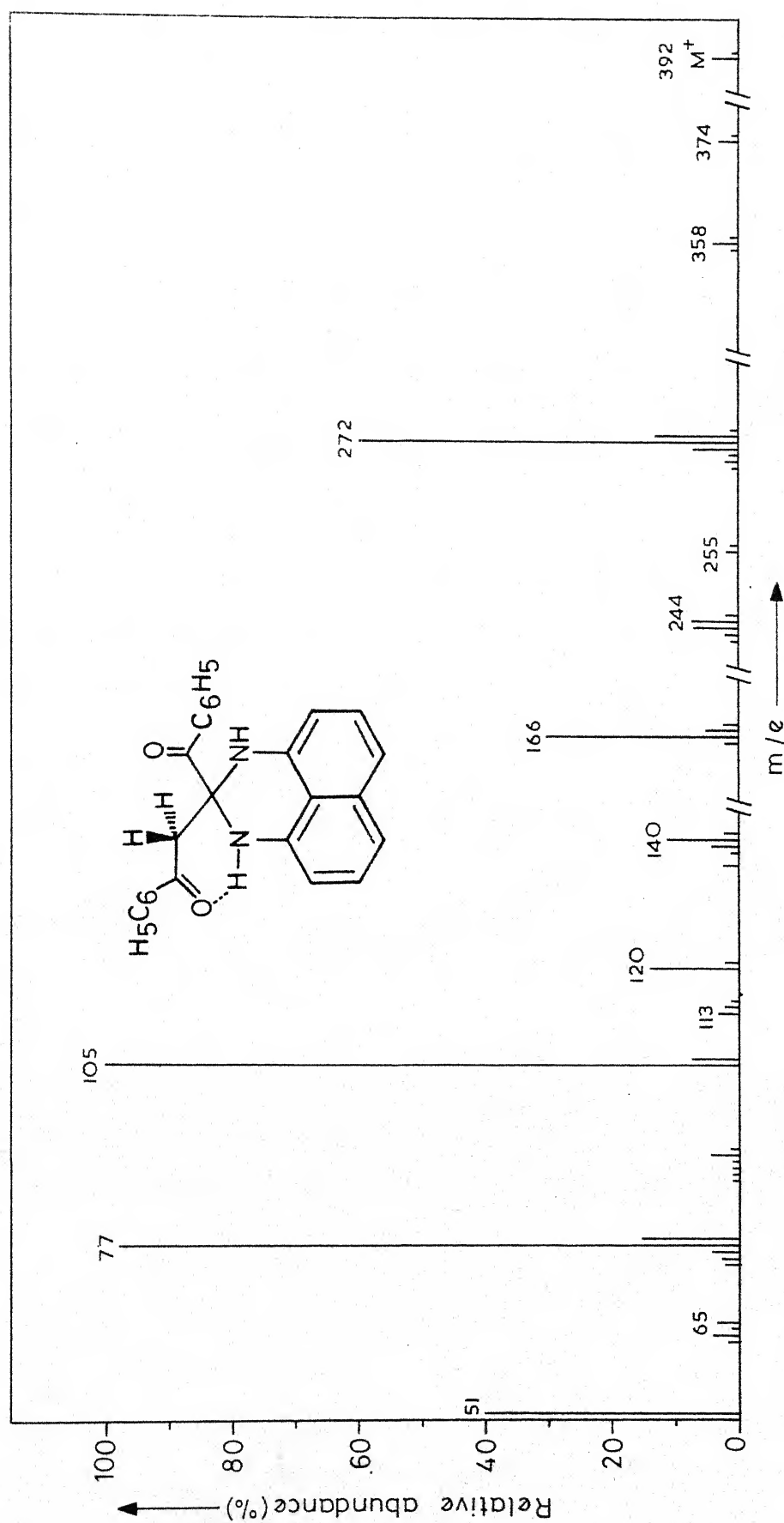
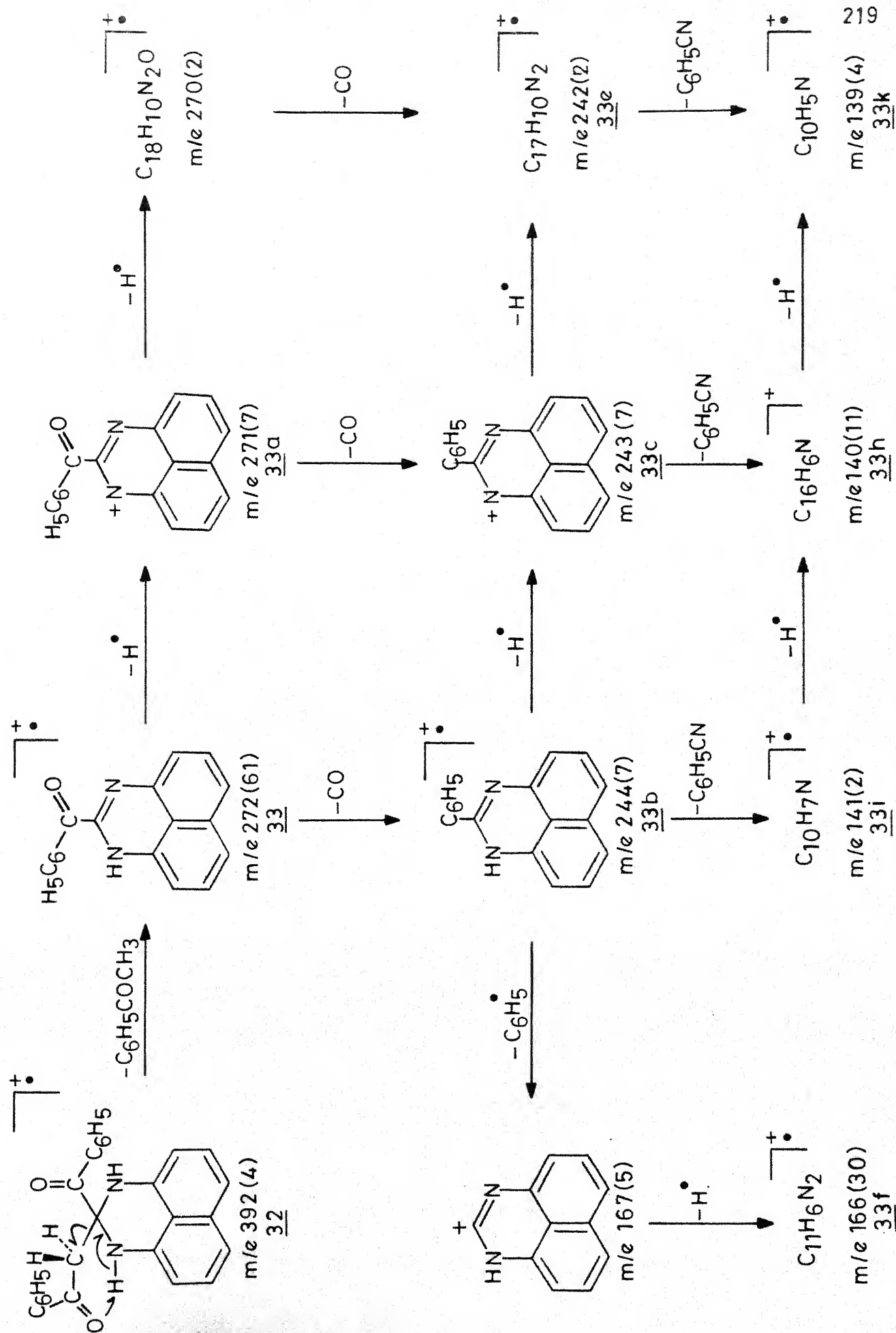
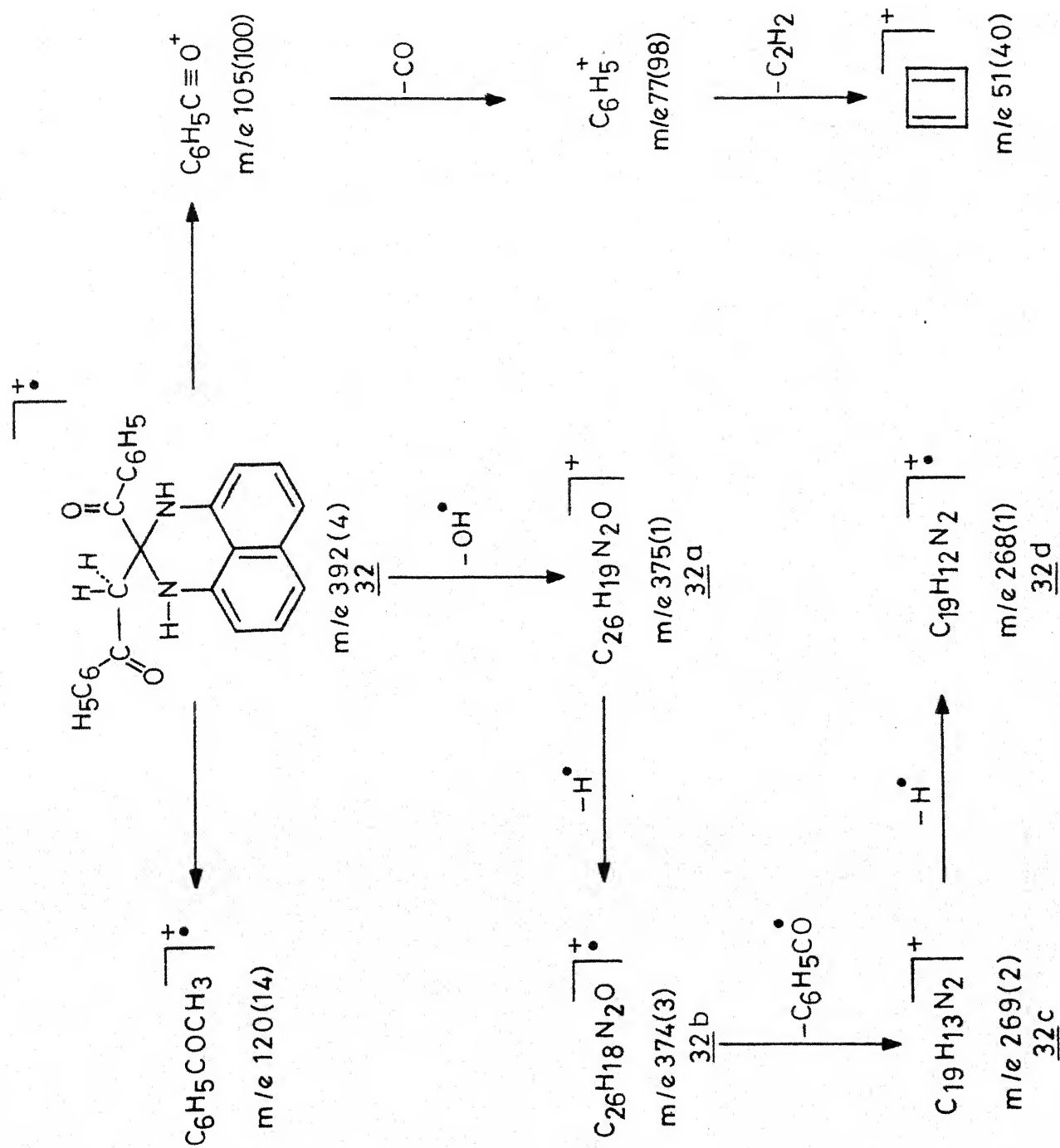


Fig. III.17 Mass spectrum of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine (32)

Scheme III.17

Scheme III.17 (contd)



Further to our studies, we have examined the reaction of 2-aminopyridine with DBA. The reaction of 2-aminopyridine with DBA gave a mixture of two 1:1 adducts consisting of 2-(2-imino-1-(2H)-pyridyl)-1,4-diphenylbut-2-ene-1,4-dione (34) and 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35). The structures of both 34 and 35 were established on the basis of analytical results and spectral data.

The ir spectrum of 34, for example, showed a band at  $3115\text{ cm}^{-1}$ , characteristic of an NH stretching frequency and two bands at  $1668$  and  $1653\text{ cm}^{-1}$ , respectively, due to two carbonyl groups. The nmr spectrum of 34 (Fig. III.18), showed several multiplets at  $5.96\delta$  (1H),  $6.63\delta$  (2H),  $7.53\delta$  (11H) and two singlets at  $7.0\delta$  (1H) and  $7.13\delta$  (1H). Of these, the multiplet around  $5.96\delta$  is assigned to the  $H_5$ -proton of the pyridine ring, which is the most shielded proton. The multiplet around  $6.63\delta$  can be assigned to the  $H_3$  and  $H_4$  protons of the pyridine ring, whereas the signal at  $7.13\delta$  could be assigned to the  $H_6$ -proton of the pyridine ring. The complex multiplet centred around  $7.53\delta$  could be assigned to the aromatic protons of the two benzoyl groups and the NH proton. The singlet at  $7.03\delta$  is assigned to the vinylic proton in 34.

The mass spectrum of 34 (Fig. III.19) showed a molecular ion peak at  $m/e$  328 (40), which undergoes the loss of an NH fragment to give the ion 34a at  $m/e$  313 (7).



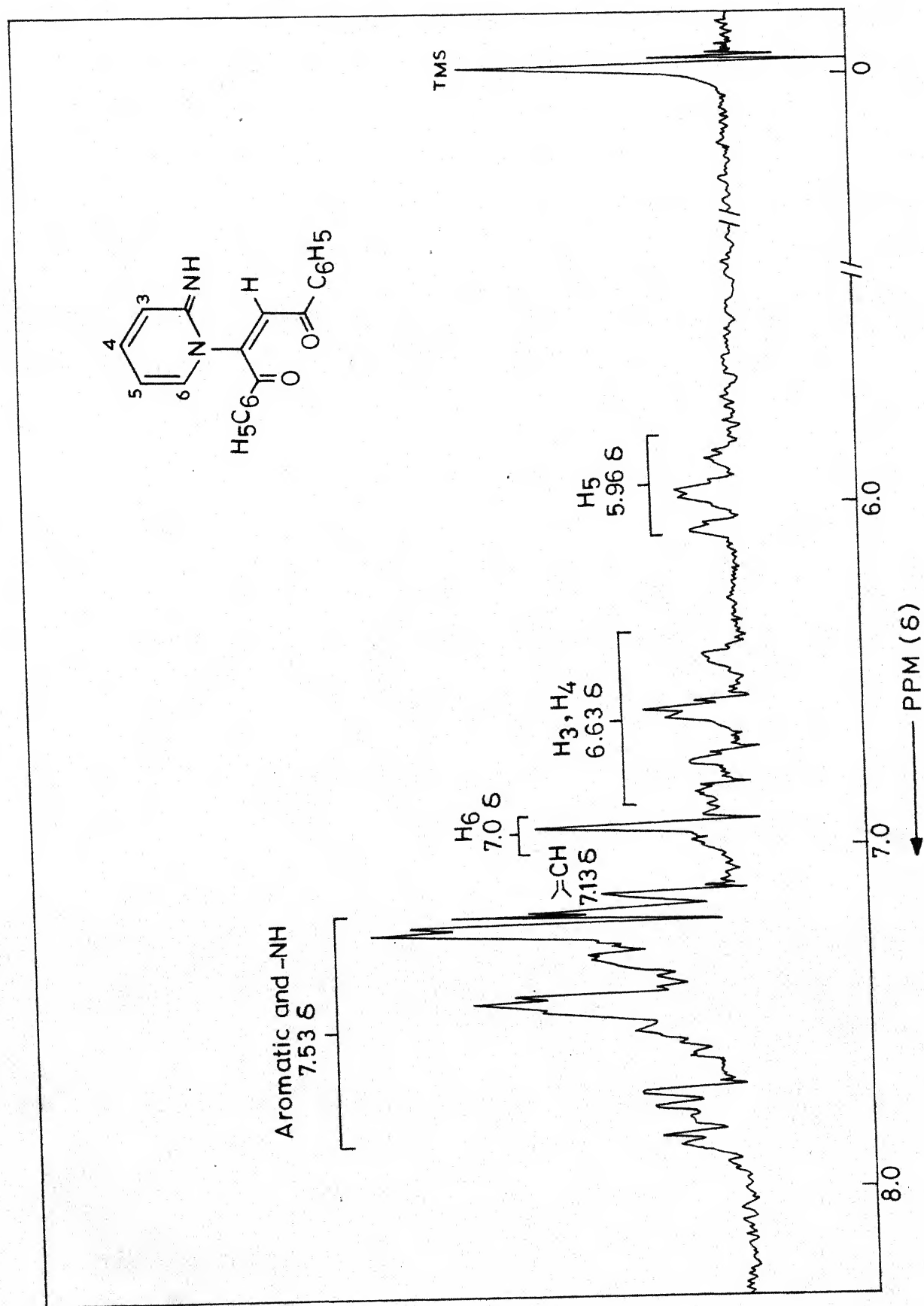


Fig. III.18 NMR spectrum (60 MHz) of 2-(2-imino-1(2H)-pyridyl)-1,4-diphenylbut-2-ene-1,4-dione (34)

Similar nitrene eliminations from 2-aminopyridine derivatives are reported in the literature.<sup>44,45</sup> A pericyclic transformation of the dibenzoylalkene function will lead to 34b, which in turn can undergo elimination of fragments like  $\text{CO}_2$ , CO and  $\text{C}_6\text{H}_5$  to give the ions 34c, at  $m/e$  284 (9), 34d, at  $m/e$  300 (10) and 34e, at  $m/e$  251 (20), respectively. Further elimination of a CO group from 34e can lead to the fragment 34f at  $m/e$  223 (100). Elimination of HCN from the molecular ion 34, however, will lead to the fragment 34i at  $m/e$  301 (8). The peaks at  $m/e$  105 (61), 78 (66), and 77 (37) can be attributed to benzoyl, pyridyl and phenyl fragments, respectively. Other peaks in the spectrum of 34 were observed at  $m/e$  222 (12), 221 (32), 209 (25), 207 (53), 195 (24), 181 (22), 121 (13), 91 (8) and 51 (15). Some of the possible pathways for the formation of these fragments are shown in Scheme III.18.

The ir spectrum of 35 showed two absorption bands at 3160 and  $1710\text{ cm}^{-1}$ , which have been assigned to a hydrogen-bonded NH and CO group, respectively. The uv spectrum of 35 showed two absorption maxima at 258 and 380 nm, characteristic of enamine diones (see, Table III.2).

The nmr spectrum of 35 (Fig. III.20) showed a sharp singlet at  $6.22\delta$  (1H), which is assigned to the vinylic proton. In addition, the spectrum showed several multiplets

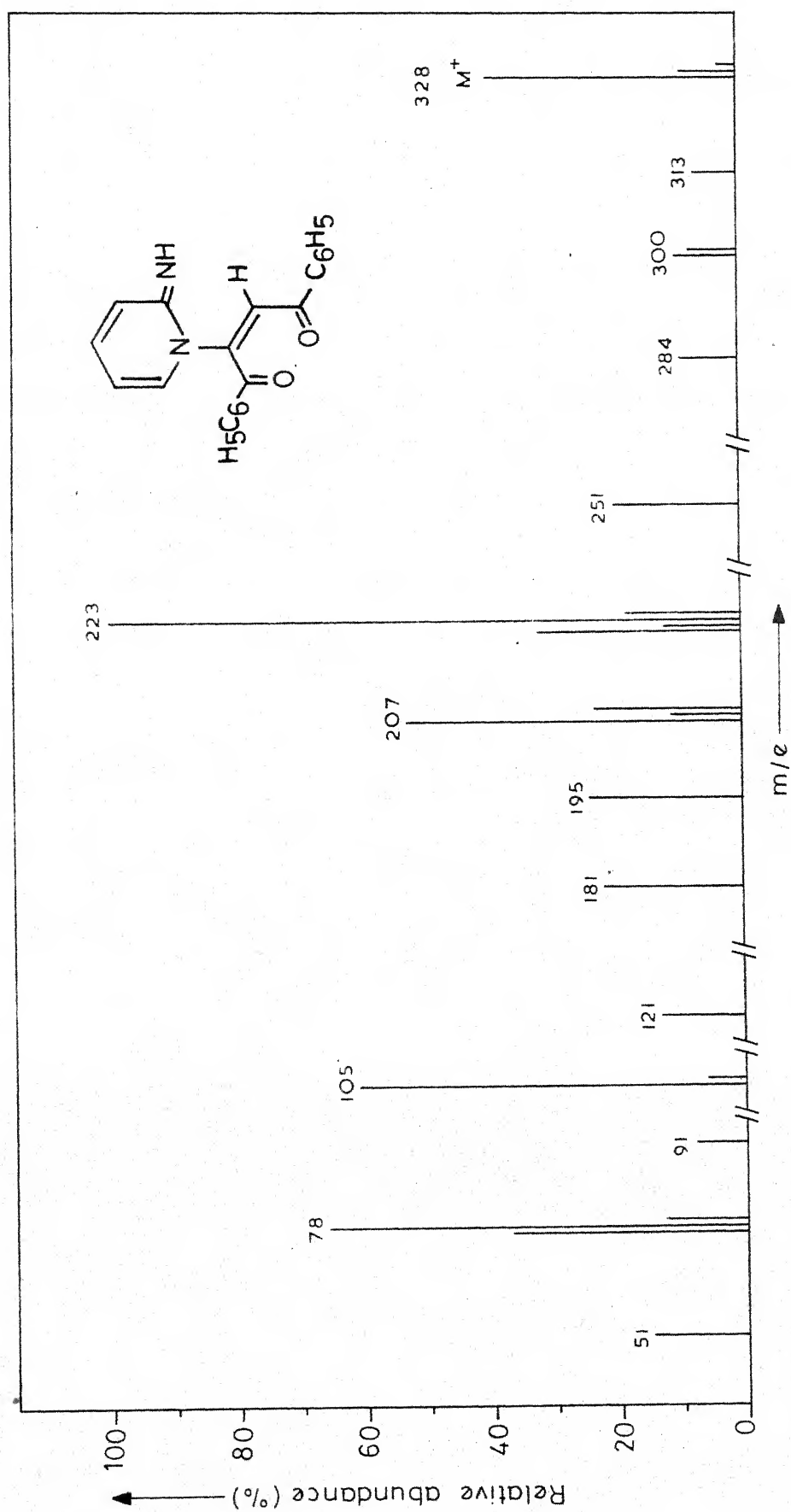
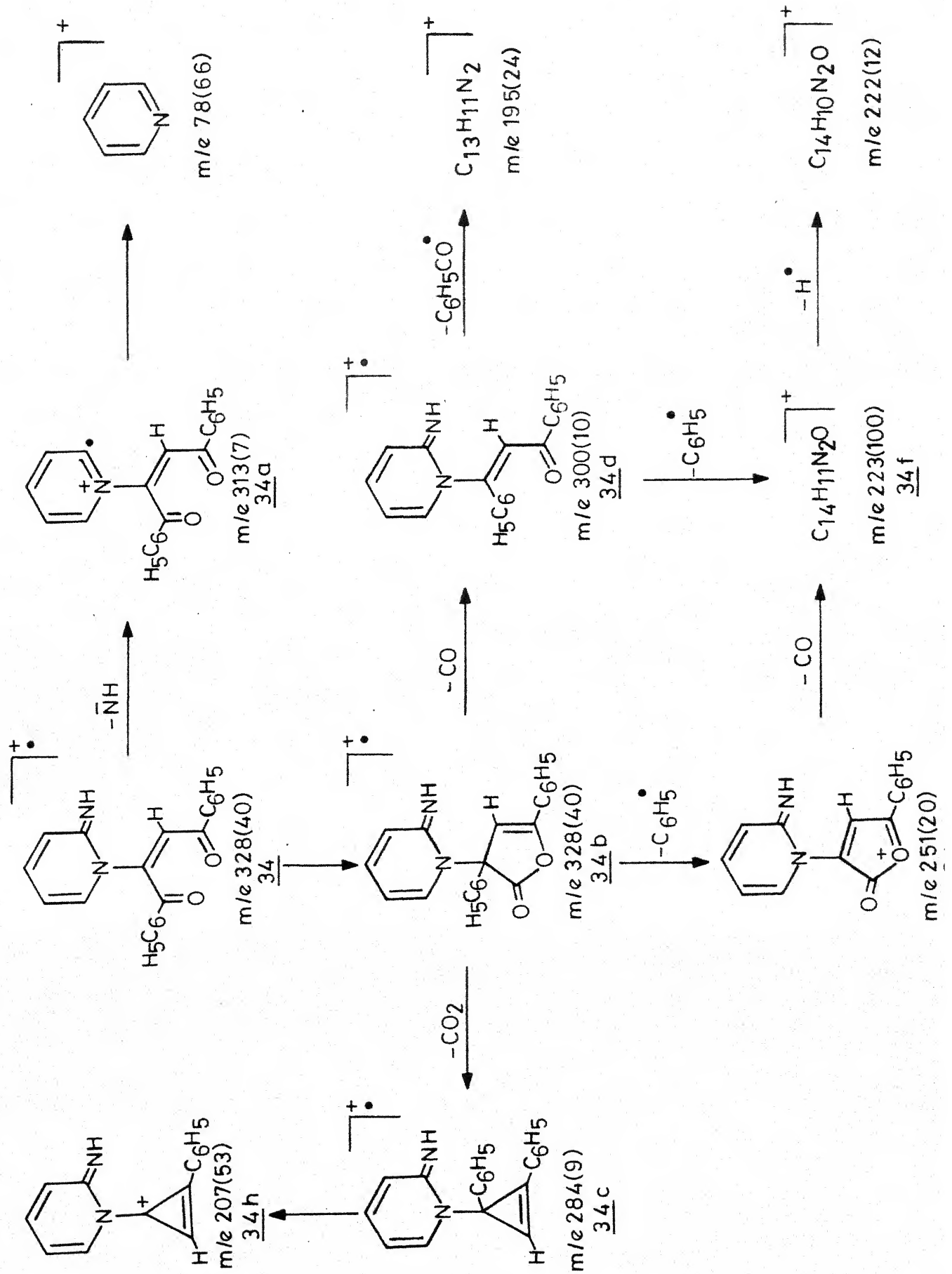


Fig. III.19 Mass spectrum of 2-(2-imino-1(2H)-pyridyl)-1,4-diphenylbut-2-ene-1,4-dione(34)

Scheme III.18





centred around  $6.83\delta$  (2H),  $7.35\delta$  (7H) and  $7.95\delta$  (5H). Of these the multiplet around  $6.83\delta$  is assigned to the most shielded protons of the pyridine ring namely, the  $H_3$  and  $H_5$  protons. The multiplets at  $7.35\delta$  and  $7.95\delta$  are assigned to the aromatic protons of the two benzoyl groups and also the  $H_4$  and  $H_6$  protons of the pyridine ring. The broad band around  $12.87\delta$  in the spectrum of 35 is assigned to the NH proton and it has been observed that this proton is exchangeable with  $D_2O$ .

A probable route to the formation of the adducts 34 and 35 in the reaction of 2-aminopyridine with DBA is shown in Scheme III.19. In the reaction of a bifunctional nucleophile like 2-aminopyridine, two modes of reaction are possible. In one case, the primary amine centre can initiate the nucleophilic attack and lead to the formation of the adduct 35. Such a reaction is analogous to the reaction of aniline and other primary amines with DBA. In the alternative mode of reaction, the tertiary amine centre of the pyridine nucleus initiates the nucleophilic attack, leading to the formation of the zwitterionic intermediate 36, which can then undergo an intramolecular transfer of a proton to give rise to the adduct 34 (Scheme III.19). It might be pointed out in this connection that the reactions of 2-aminopyridine with acrylic ester<sup>46</sup> and methyl propiolate<sup>47-49</sup> are known to proceed in a similar manner, as shown in Scheme III.20.

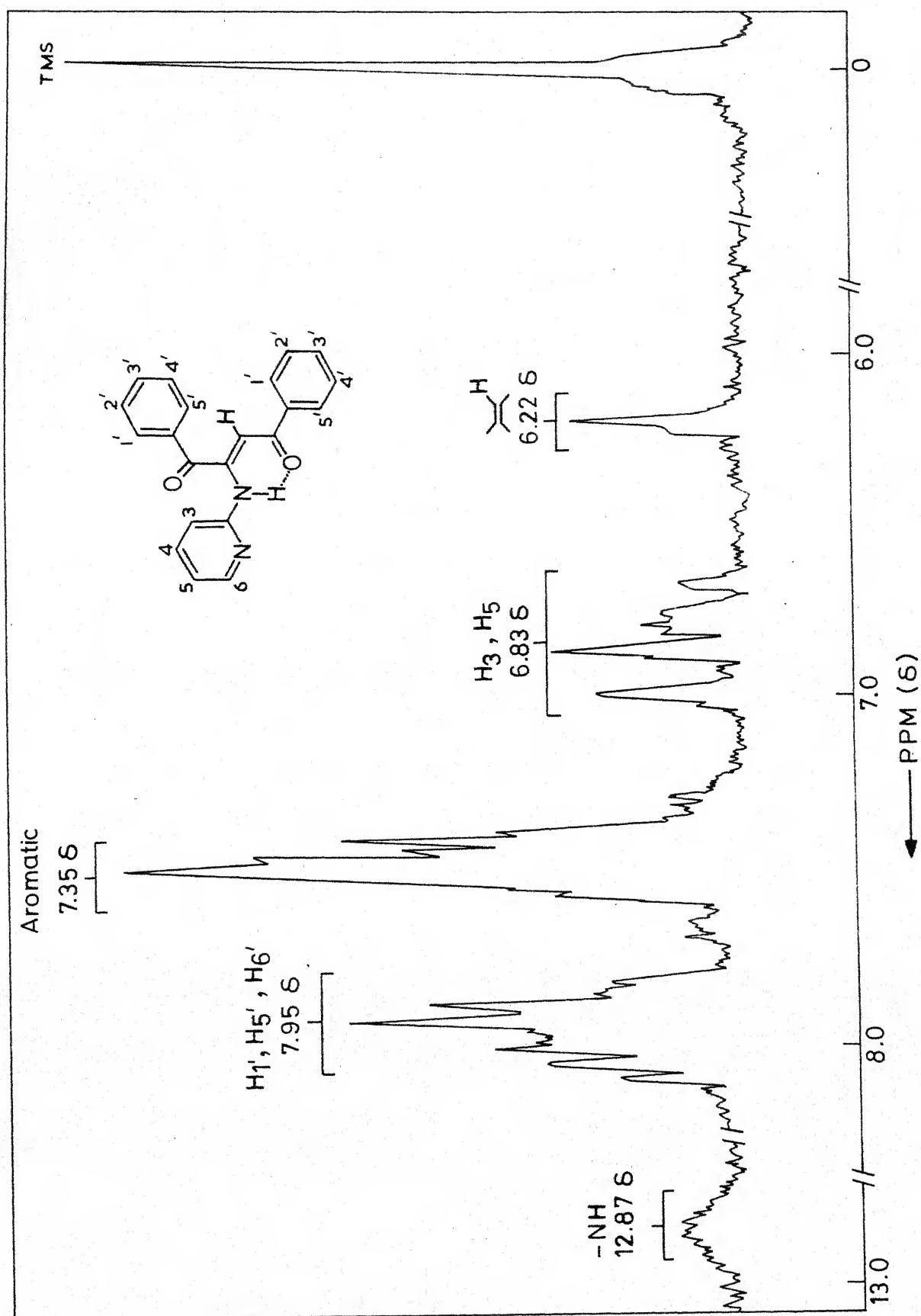
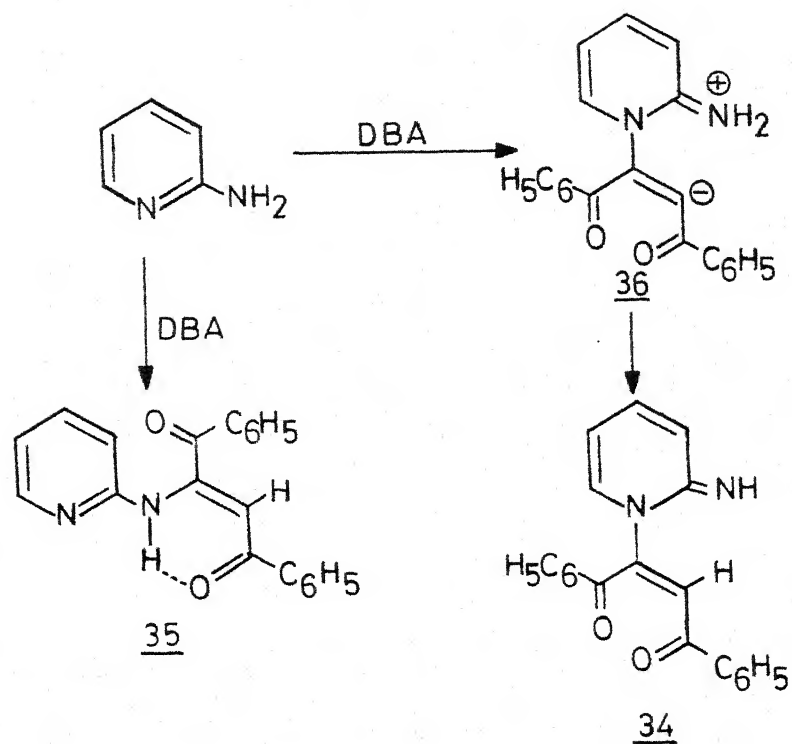
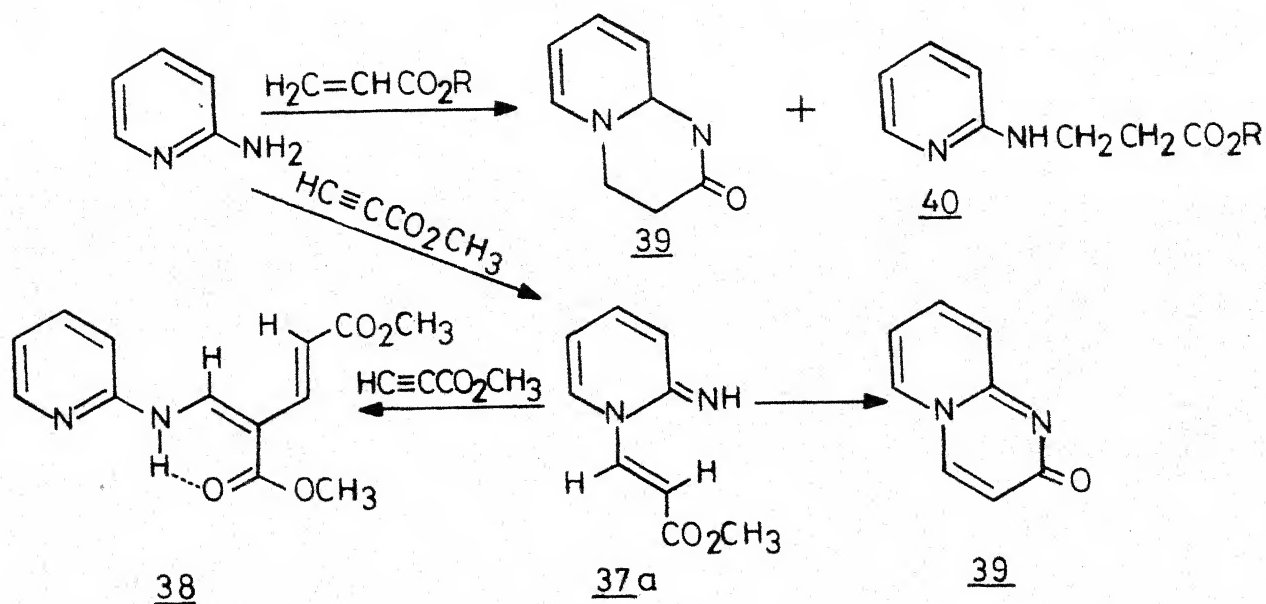


Fig.III.20 NMR spectrum(60MHz) of 1,4 -diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione(35)

Scheme III.19



Scheme III.20





### III.3.4 Electron-Impact Induced Fragmentations of Some Enamine Diones

In Chapter I of this thesis we studied the electron-impact induced transformations of some cis-1,2-dibenzoyl-alkenes and have shown that different modes of fragmentation occur in these systems. One of these modes involves an initial pericyclic transformation of the dicarbonyl-alkene function, which is then followed by other fragmentation pathways. In view of our general interest in the thermal and electron-impact transformation of 1,2-dibenzoyl-alkenes, we have examined the mass spectral fragmentation modes of some of the enamine diones that we have prepared during the course of the present studies. These include 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5), 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6), 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (7), 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione (8), 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35) and 2,3-dibenzoyl-1,4-diphenylpyrrole (11).

The mass spectrum of 5 (Fig. III.21) showed a molecular ion peak at  $m/e$  327 (13). The most intense peak at  $m/e$  222 (100) can be formed through the loss of a  $C_6H_5CO$  moiety from the molecular ion and is assigned to the fragment 5a. Subsequent loss of fragments like  $H_2O$  and  $C_6H_5$  from 5a can lead to fragments 5c and 5d at  $m/e$  204 (3) and 144 (6), respectively. Other peaks in the

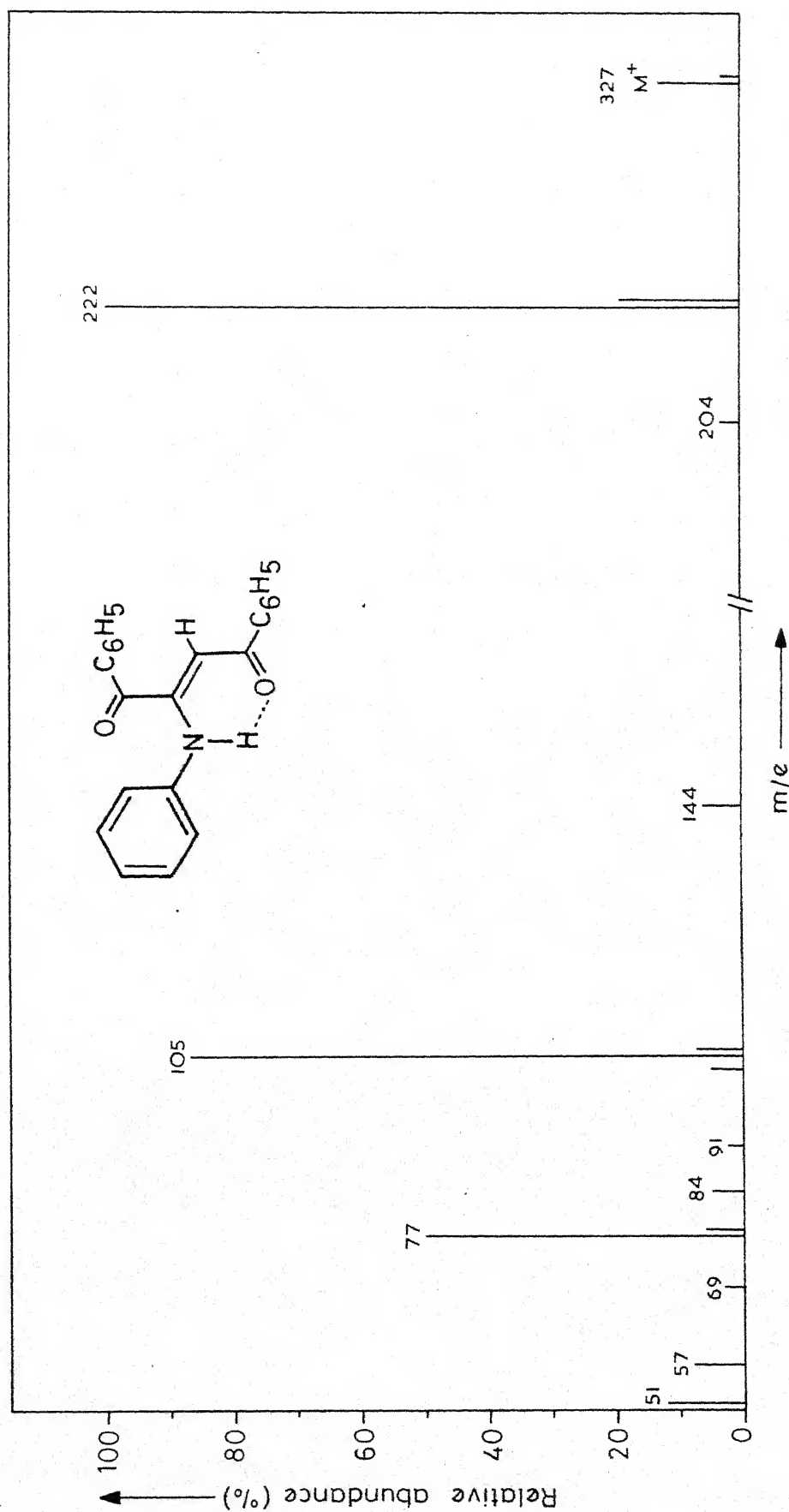
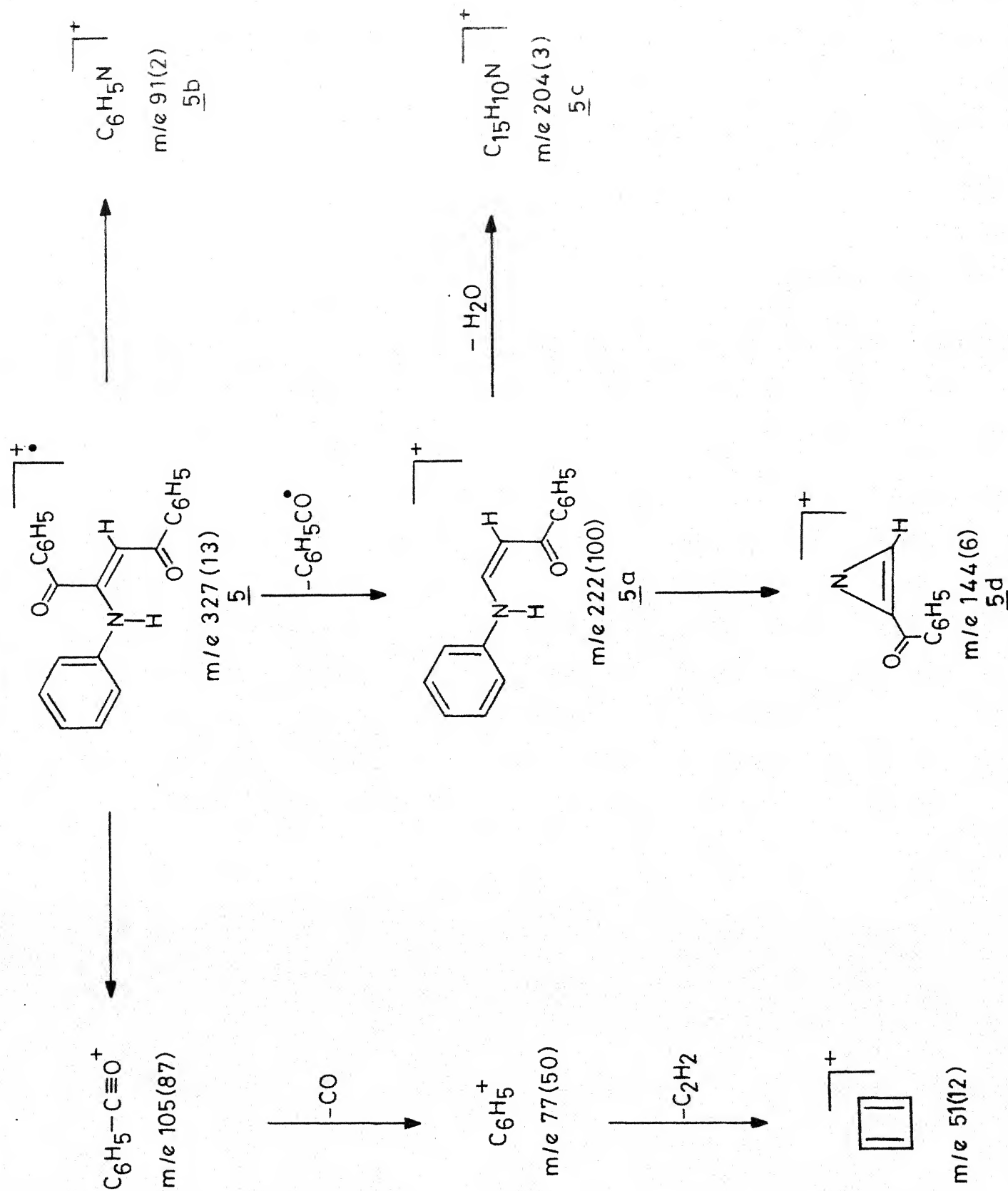


Fig.III.21 Mass spectrum of 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5)

Scheme III.21



spectrum of 5 were observed at  $m/e$  105 (87), 103 (5), 91 (2), 84 (5), 78 (6), 77 (50), 69 (3), 57 (8) and 51 (12) and some of the possible fragmentation modes are shown in Scheme III.21.

The molecular ion peak at  $m/e$  319 (100) was found to be the most abundant peak in the mass spectrum of 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6) (Fig. III.22). Of the several peaks, the ones at  $m/e$  302 (12) and 291 (18) could be assigned to fragments 6f and 6d, respectively, formed by the elimination of OH and CO fragments from the molecular ion peak. One of the likely transformations of 6 under electron-impact is its rearrangement to 6a through a pericyclic reaction. The peaks at  $m/e$  318 (7) and 242 (1) in the mass spectrum can be rationalized in terms of the loss of a hydrogen atom and  $C_6H_5$  group, from 6a to give the fragments 6c and 6b, respectively. Other peaks in the spectrum of 6 were observed at  $m/e$  303 (4), 301 (4), 290 (13), 274 (4), 214 (57), 200 (2), 196 (2), 191 (2), 186 (12), 146 (6), 131 (2), 112 (19), 105 (27), 91 (3), 84 (14), 83 (4), 78 (5), 77 (27), 69 (13), 62 (4), 55 (4), 53 (2) and 51 (10), which may be due to some of the fragments shown in Scheme III.22.

The mass spectrum of 1,4-diphenyl-2-(N-phenylbenzyl-amino)but-2-ene-1,4-dione (8) (Fig. III.23) showed the molecular ion peak at  $m/e$  417 (55). Other peaks in the

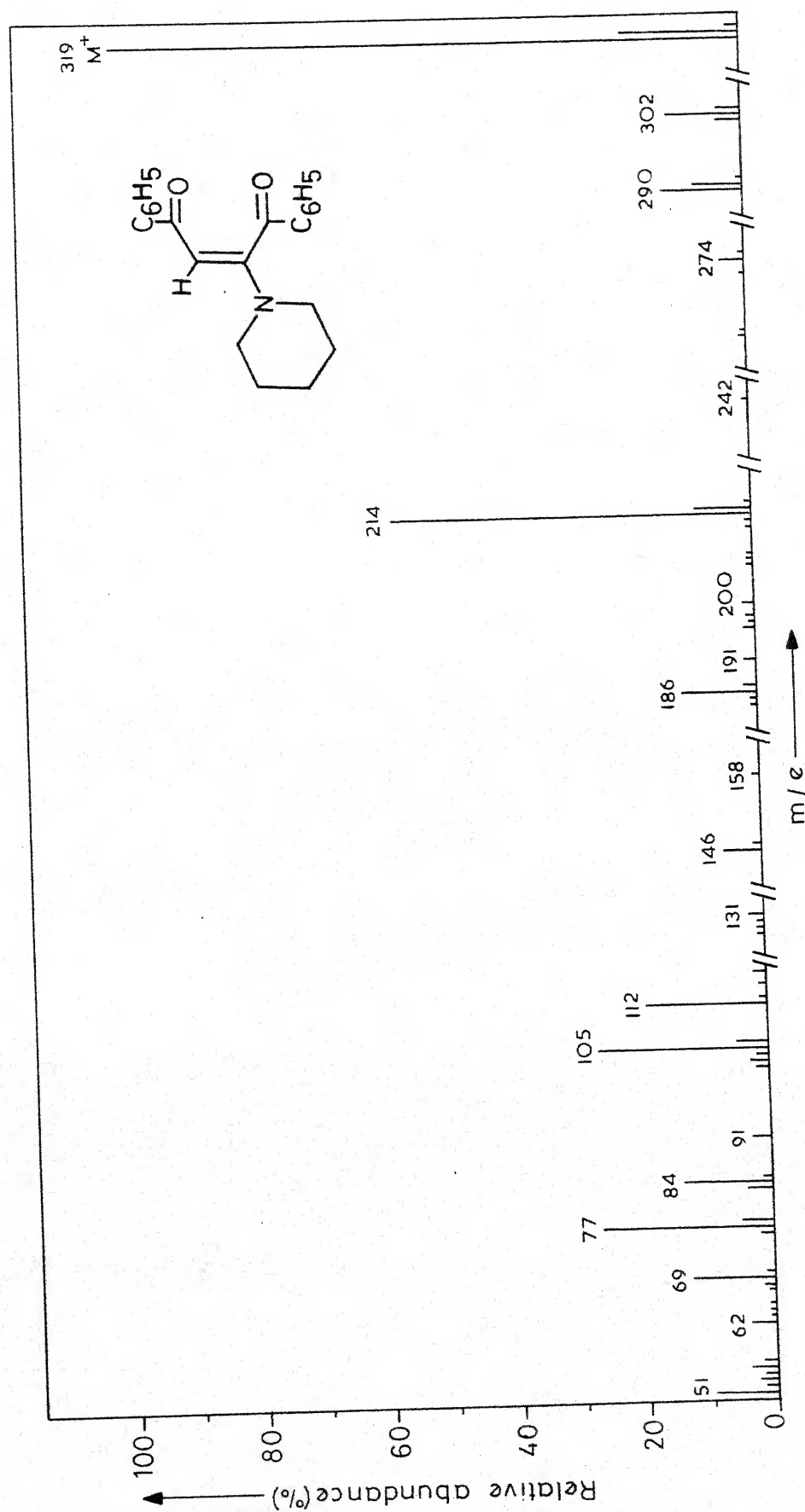
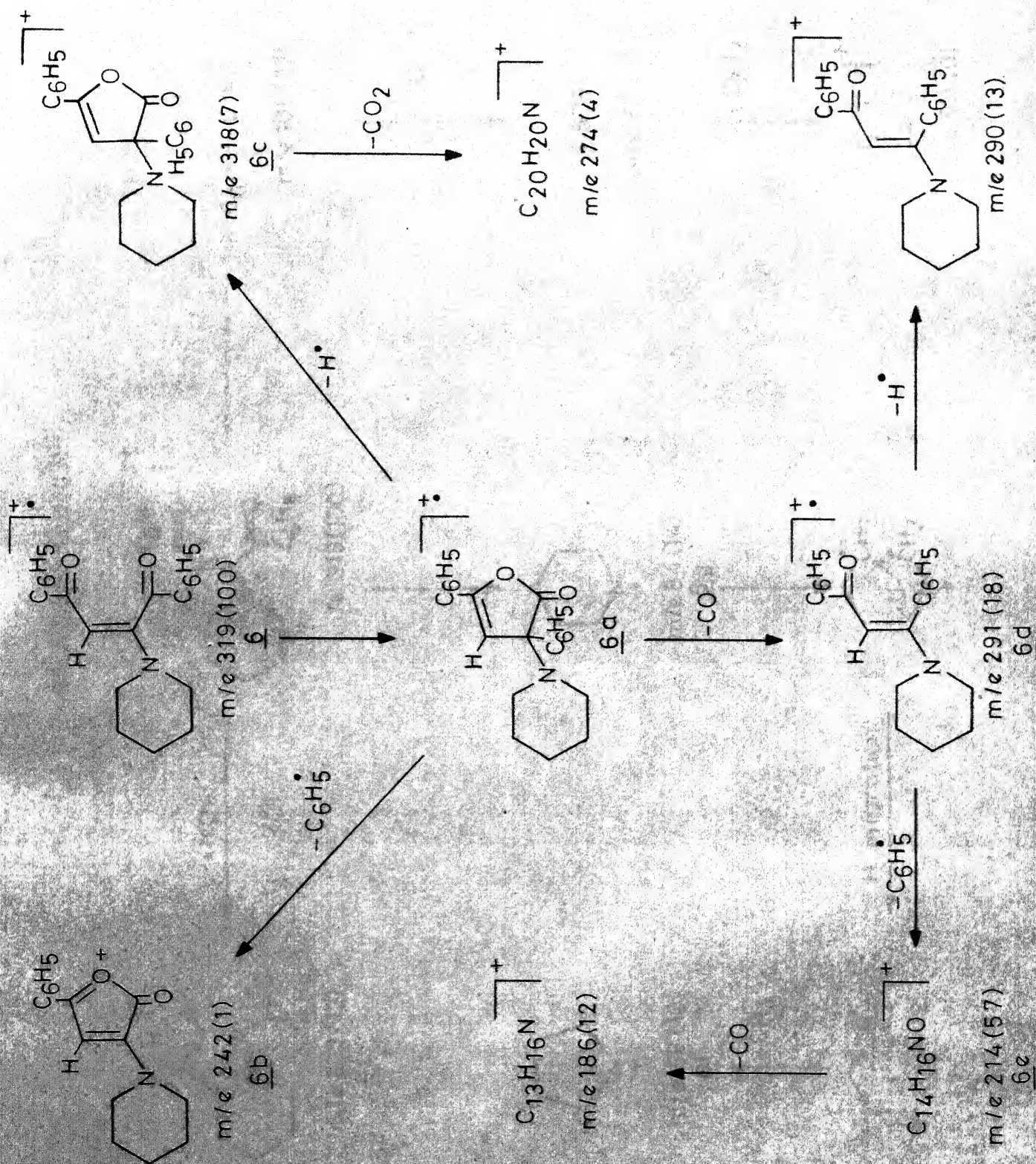


Fig.III.22 Mass spectrum of 1,4-diphenyl 1-(2-piperidinobut-2-en-1-yl)-1,4-dione (6)

Scheme III. 22







spectrum were observed at  $m/e$  340 (2), 312 (100), 311 (8), 250 (3), 236 (25), 182 (9), 181 (7), 180 (5), 179 (3), 178 (3), 167 (3), 159 (2), 131 (3), 91 (19), 64 (4), 63 (10), 62 (11), 52 (42) and 51 (32). Some of the probable fragmentation modes are shown in Scheme III.23. One of the prominent modes of fragmentation involves the loss of a phenyl group from the molecular ion to give a fragment at  $m/e$  340 (2), which can subsequently lose a CO fragment to give the ion at  $m/e$  312 (100). On the basis of the electron-impact fragmentations of other enamine diones that we have examined, it is reasonable to assume that the molecular ion 8, undergoes an initial pericyclic transformation to give an intermediate, which loses a  $C_6H_5$  fragment to give the ion 8a at  $m/e$  340. Further loss of a CO group from 8a will lead to the ion 8b at  $m/e$  312. The presence of a peak at  $m/e$  236 (25) is attributed to the fragment 8d, formed through a fragmentation of the molecular ion and proceeding through a hydrogen migration. Similarly, the strong peak at  $m/e$  78 (89) can be assigned to the benzene radical ion, 8i, formed through a fragmentation process, proceeding through a hydrogen-transfer. The presence of a high-intensity peak at  $m/e$  105 (92) is assigned to the benzoyl fragment, formed through a simple  $\alpha$ -cleavage of 8.



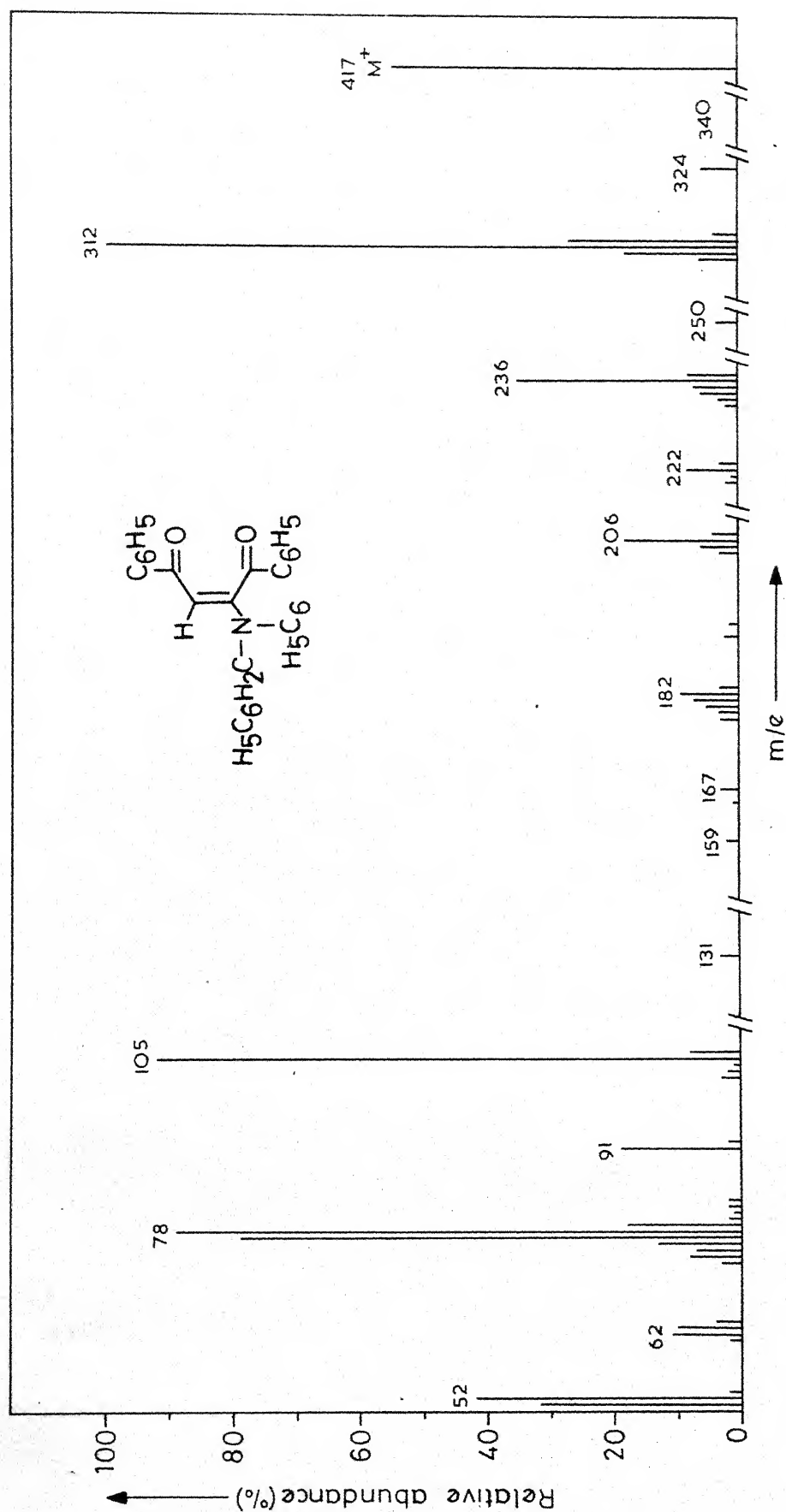
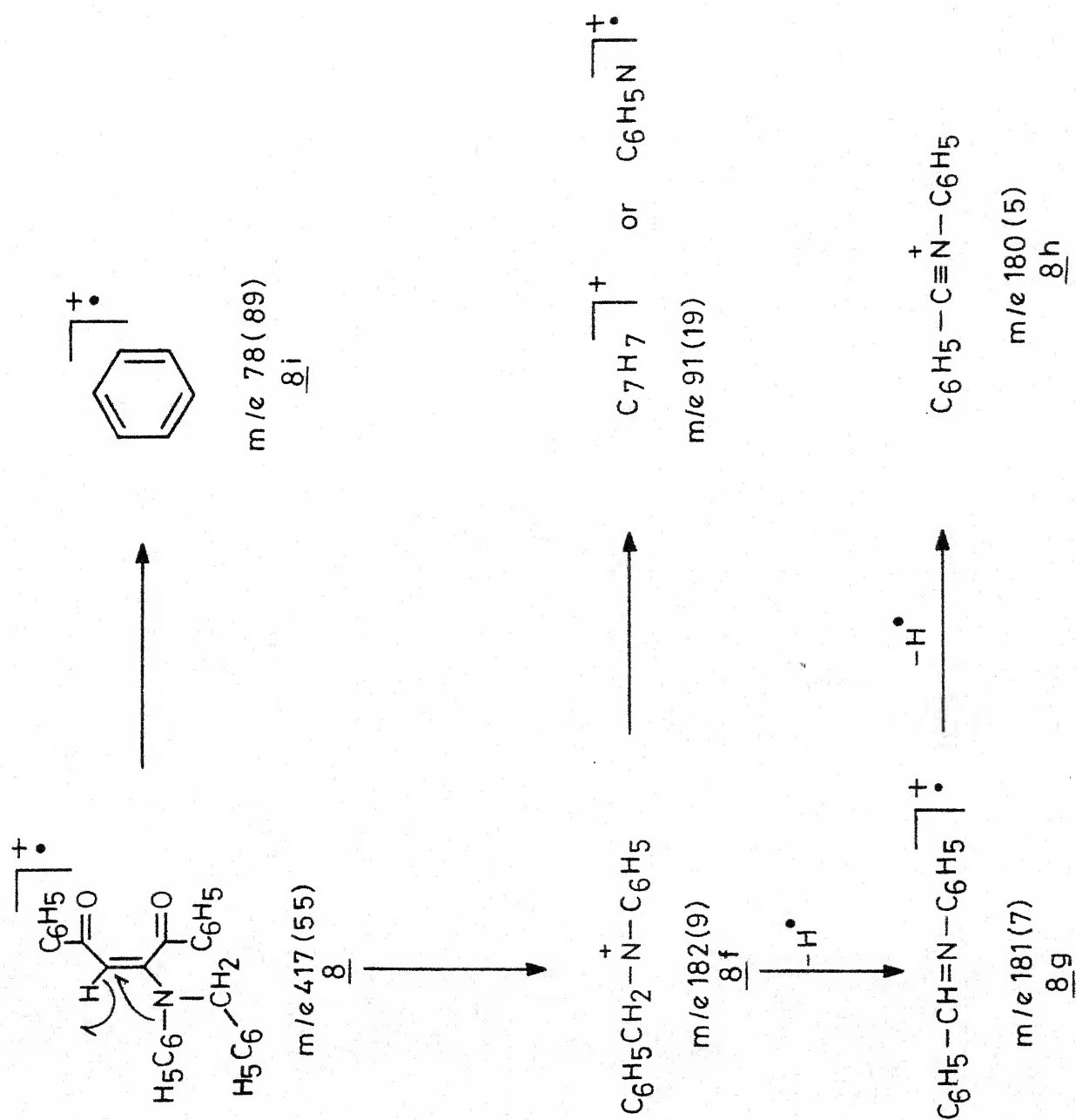


Fig.III.23 Mass spectrum of 1,4-diphenyl-2-(N-phenylbenzylamino)but-2-ene-1,4-dione(8)



Scheme III.23(contd)



The mass spectrum of 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (7) (Fig. III.24) showed a low-intensity peak at  $m/e$  343 (7), assigned to the molecular ion peak. Other peaks in the spectrum were observed at  $m/e$  326 (1), 325 (2), 238 (100), 237 (1), 221 (10), 220 (32), 192 (2), 165 (2), 160 (4), 105 (65), 77 (48), 65 (4) and 51 (9). Some of the probable fragmentation modes are shown in Scheme III.24. The highest intensity peak in the spectrum of 7 was observed at  $m/e$  238 (100), which can be assigned to the fragment 7a, formed through the loss of a  $C_6H_5CO$  group from the molecular ion. Further loss of a hydrogen atom from 7a will give rise to the fragment 7b at  $m/e$  287, which in turn can lose a phenyl group to give the fragment 7c at  $m/e$  160. The loss of an OH group from the molecular ion, however, can lead to the fragment 7d at  $m/e$  326, whereas the peaks at  $m/e$  221, 220 and 192 can be rationalized in terms of the fragments 7f, 7g and 7h, formed through the successive loss of  $C_6H_5CO$ , H and CO groups, respectively from 7d.

The mass spectrum of 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35) (Fig. III.25) showed a molecular ion peak at  $m/e$  328 (1). One of the major fragmentation modes of 35 has been through the loss of a

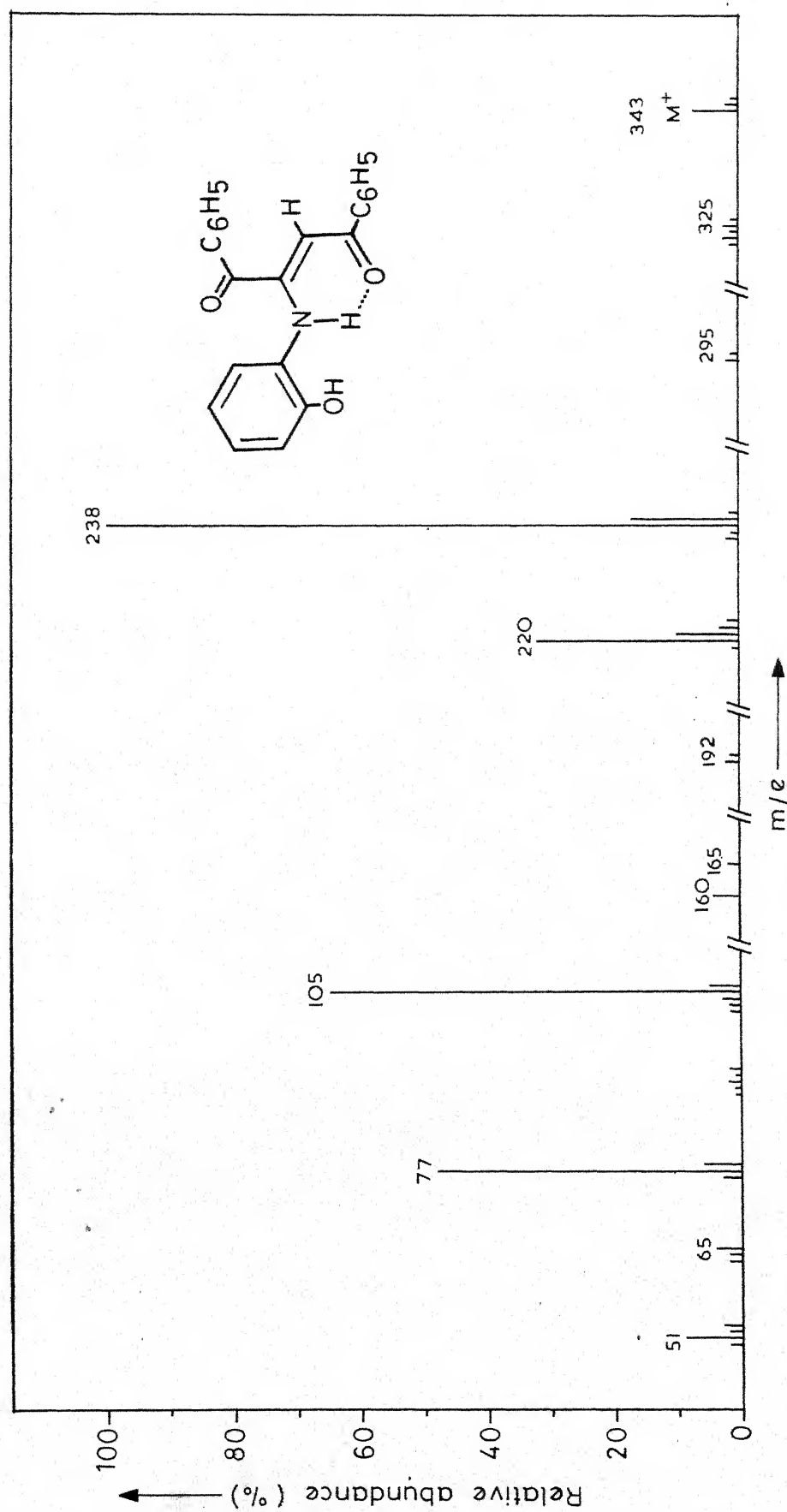
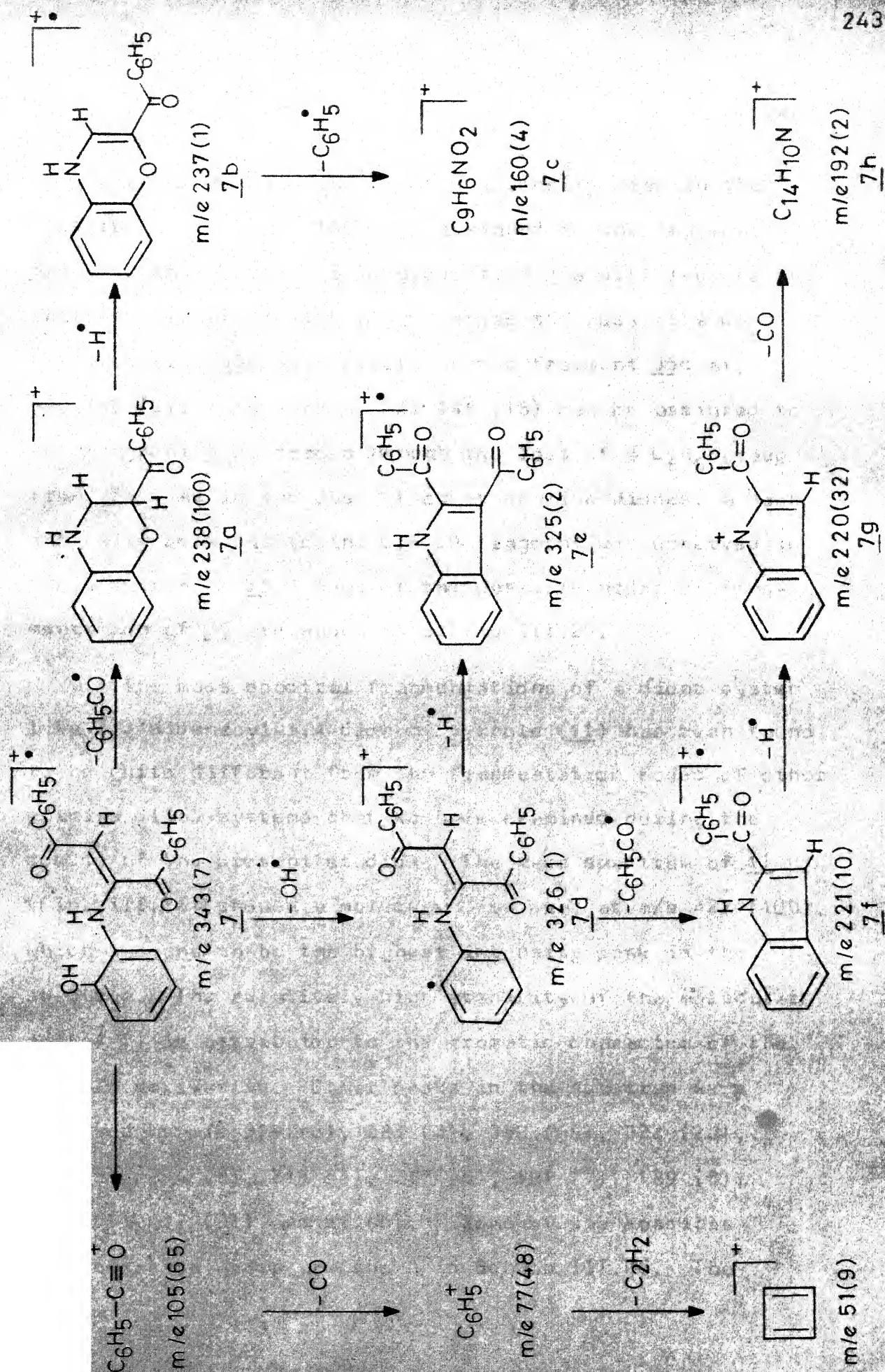


Fig.III.24 Mass spectrum of 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione(7)

Scheme III. 24



$C_6H_5CO$  group to give the highest intensity peak in the spectrum at  $m/e$  223 (100) and assigned to the fragment 35a. Further loss of a CO group from 35a will lead to the fragment 35b at  $m/e$  195 (1), whereas the loss of a  $CH_2$  fragment from 35b will result in the fragment 35c at  $m/e$  181 (2). The peak at  $m/e$  146 (15) can be assigned to the fragment 35d, formed through the loss of a  $C_6H_5$  group from 35a. As in the case of other enamine diones, a high intensity peak due to the  $C_6H_5CO$  fragment was observed in the spectrum of 35. Some of the possible modes of fragmentation of 35 are shown in Scheme III.25.

The mass spectral fragmentations of a dione system like 2,3-dibenzoyl-1,4-diphenylpyrrole (11) has been found to be quite different from the fragmentation modes of other enamine dione systems that we have examined during the course of the present studies. The mass spectrum of 11 (Fig. III.26) showed a molecular ion peak at  $m/e$  427 (100), which happens to be the highest intensity peak in the spectrum. The relatively high stability of the molecular ion of 11 is attributed to the aromatic character of the pyrrole derivative. Other peaks in the spectrum were observed at  $m/e$  399 (3), 383 (3), 350 (66), 322 (20), 306 (5), 294 (8), 219 (4), 217 (5), 191 (7), 189 (8), 105 (61), 77 (81) and 51 (5). Some of the possible fragmentation modes are shown in Scheme III.26. The



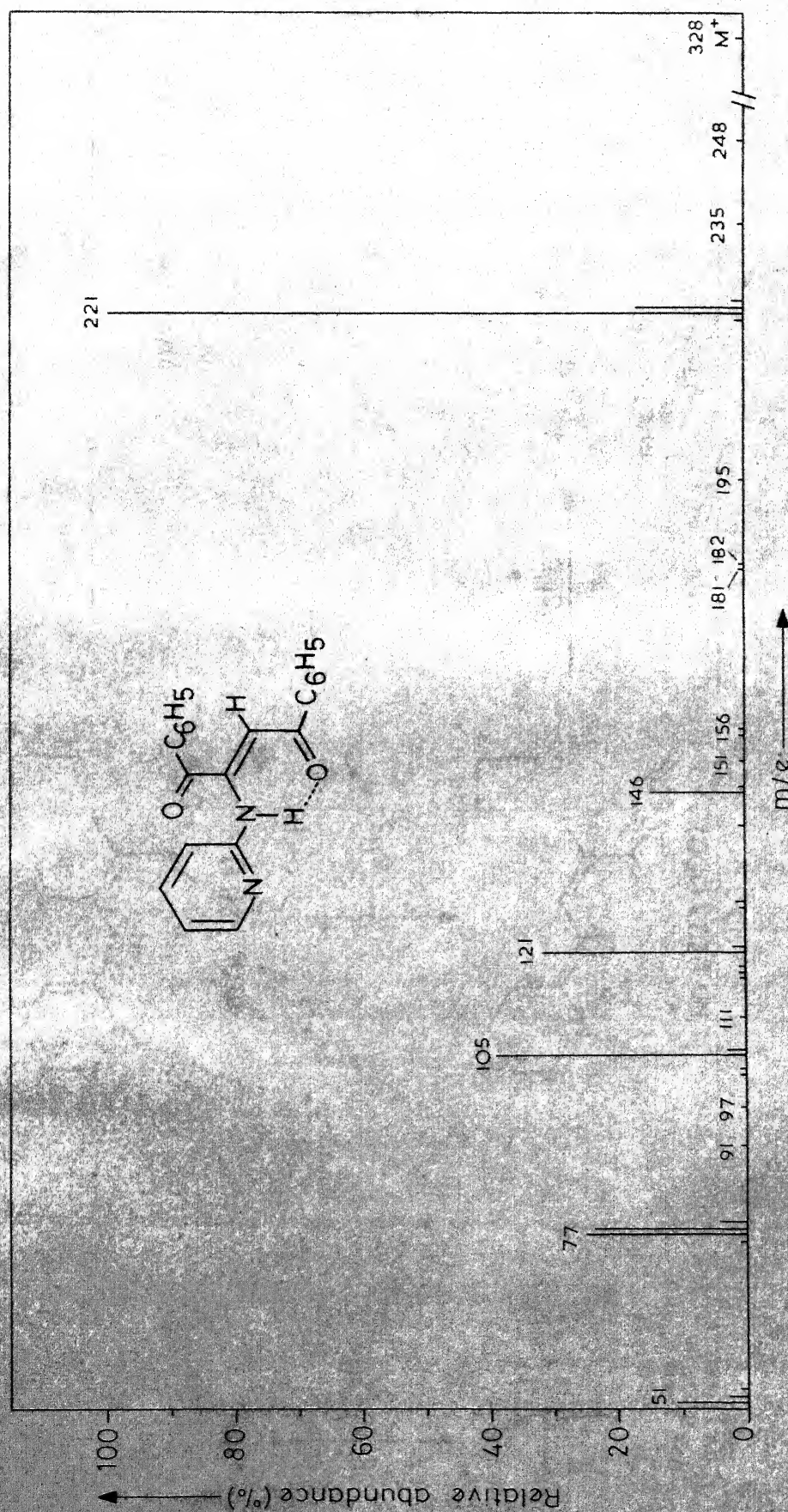
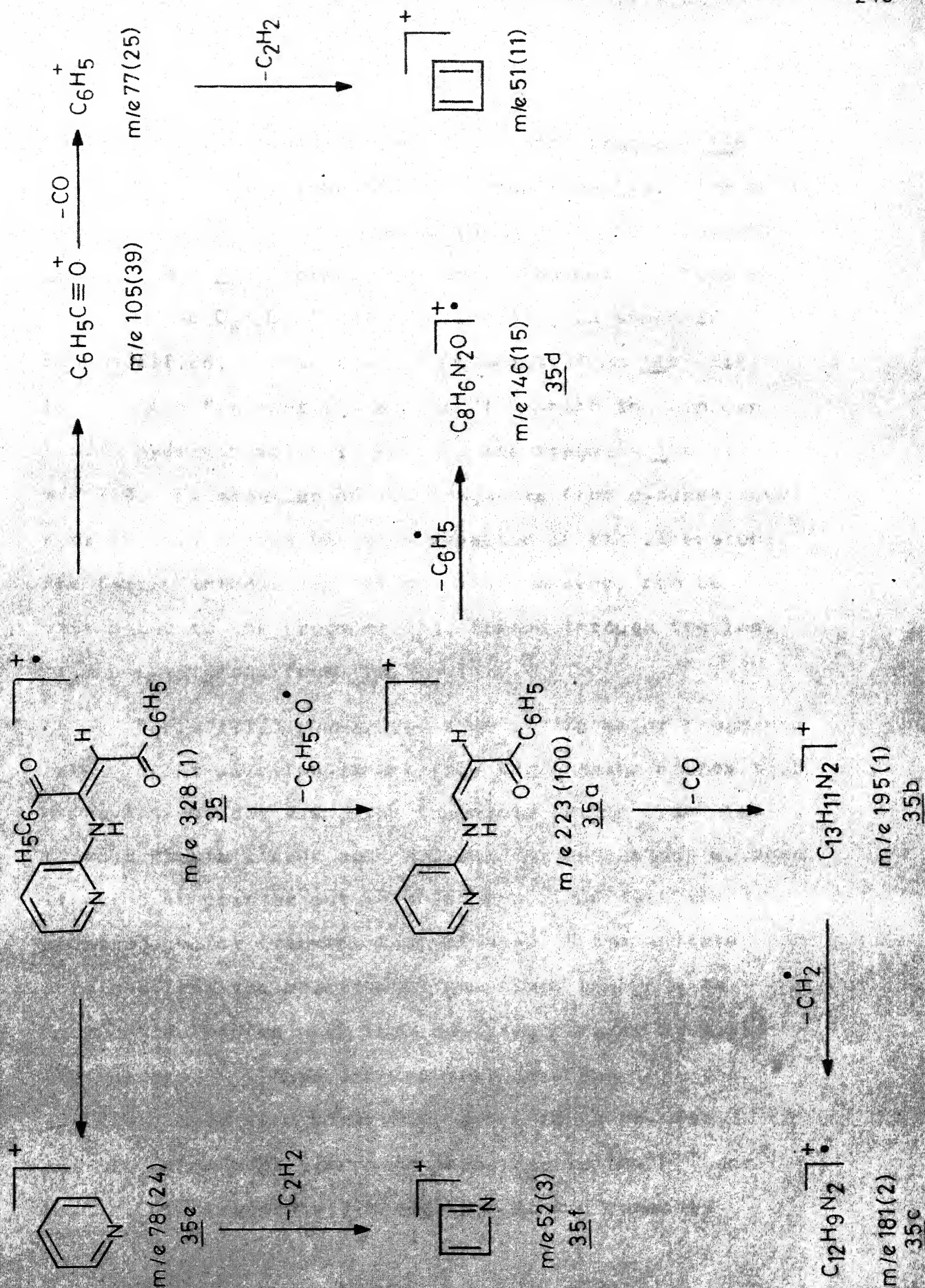


Fig.III.25 Mass spectrum of 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35)





peak at  $m/e$  399 could be assigned to the fragment 11b, formed through the loss of a CO group from 11a. The peaks at  $m/e$  322, 294 and 191 can be assigned to the fragments 11c, 11d and 11e, formed through the successive loss of  $C_6H_5$ , CO and  $C_6H_5CN$  fragments from 11b, as shown in Scheme III.26. Loss of a  $C_6H_5CN$  moiety from 11c will lead to the fragment 11g at  $m/e$  219, which in turn can lose a hydrogen molecule to give the fragment 11h at  $m/e$  217. Elimination of RCN fragments from  $\alpha$ -substituted pyrrole derivatives has been reported in the literature.<sup>50</sup> The fairly intense peak at  $m/e$  350, however, can be attributed to the fragment 11i, formed through the loss of a phenyl group from 11a.

Table III.3 summarizes some of the major fragments formed under electron-impact from the enamine diones that we have studied. Also, the fragments formed from cis-1,2-dibenzoylstilbene are included for comparison purposes. It might be pointed out in this connection that the electron-impact fragmentation of some of the adducts obtained from the reaction of secondary amines with acetylenic ketones have been reported earlier by Aplin and Hesters.<sup>51</sup> These workers have observed that the adducts formed from piperidine and morpholine, for example, show high intensity peaks due to  $(M-OH)^+$  and  $(M-C_6H_5CO)^+$  fragments, in addition to the commonly

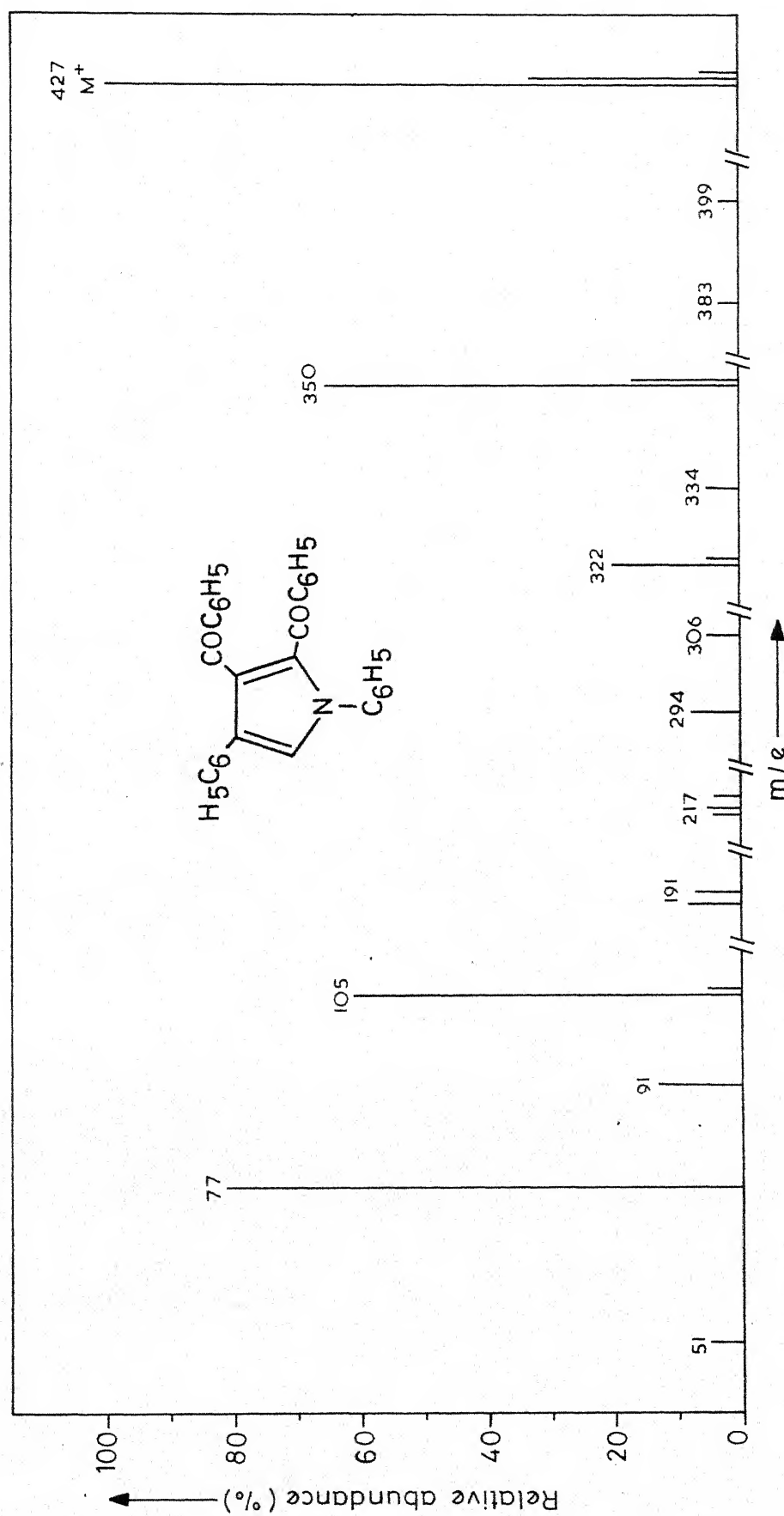


Fig.III.26 Mass spectrum of 2,3-dibenzoyl-1,4-diphenylpyrrole (11)

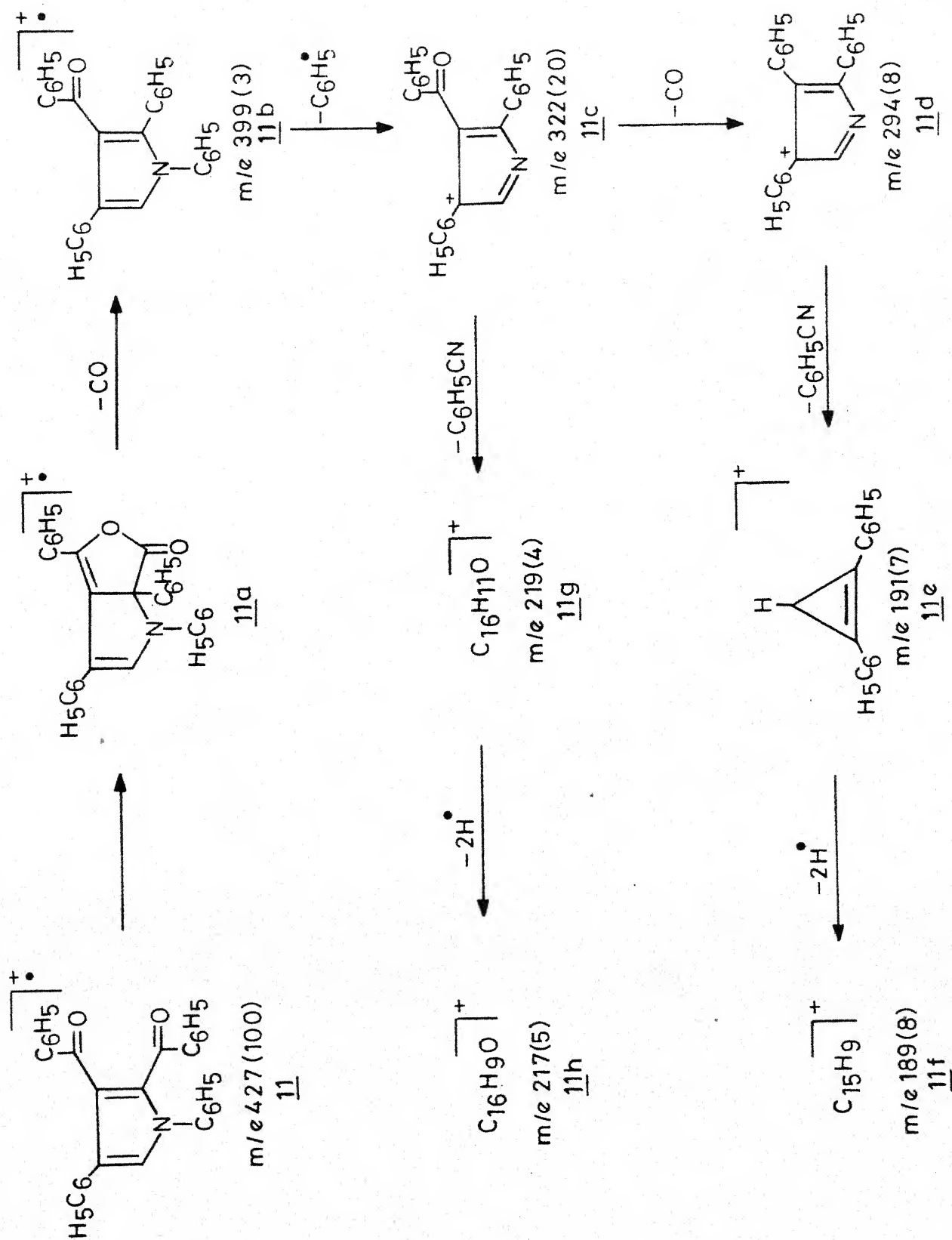




Table III.3 - Some of the Fragment Ions Formed from Enamine Diones and cis-Libenzoylstilbene Under Electron-Impact

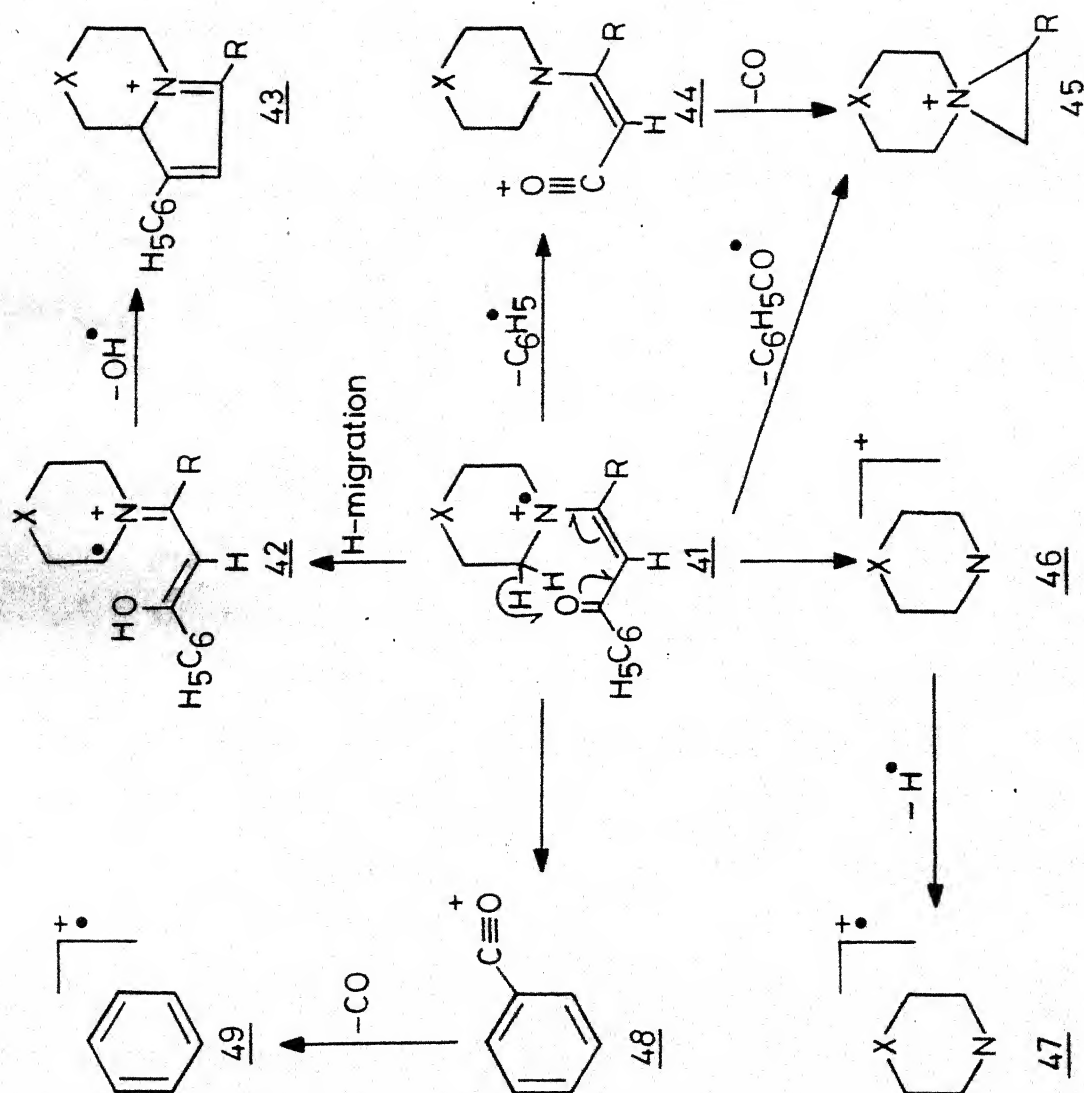
Name	M <sup>+</sup>	(M-OH) <sup>+</sup>	(M-CO) <sup>+</sup> or (M-H-CO) <sup>+</sup>	(M-CO <sub>2</sub> ) <sup>+</sup> or (M-H-CO <sub>2</sub> ) <sup>+</sup>	(N-C <sub>6</sub> H <sub>5</sub> ) <sup>+</sup>	(N-C <sub>6</sub> H <sub>5</sub> CO) <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>	C <sub>6</sub> H <sub>5</sub>	Fragments after H- abstraction
1,4-Diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5)	13	-	-	-	-	100	87	50	-
1,4-Diphenyl-2-piperidinobut-2-ene-1,4-dione (6)	100	12	8 13	1 4	1	57	27	27	-
2-(N-2-Hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione (7)	7	1	-	-	-	100	65	48	-
1,4-Diphenyl-2-(N-phenylbenzylamino)-but-2-ene-1,4-dione (8)	55	-	-	-	2	100	92	89	35
2,3-Dibenzoyl-1,4-diphenylpyrrole (11)	100	-	3	3	66	20	61	82	-
1,4-Diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione (35)	1	-	-	-	-	100	39	25	-
cis-Libenzoylstilbene (50)	28	-	5	-	6	26	100	98	-

observed fragments like  $M^+$ ,  $(M-1)^+$ ,  $(M-R)^+$  and  $R^+$ . The general fragmentation pattern of these adducts is shown in Scheme III.27. As is evident from this scheme, a major pathway for the transformation of 41 is through an intramolecular hydrogen transfer to give the intermediate 42, which can subsequently lose an OH group to give fragment 43. In the present studies, we have observed that such a hydrogen transfer takes place in the case of both 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione (6) and 2-(N-benzyl-N-phenylamino)-1,4-diphenylbut-2-ene-1,4-dione (8), adducts having accessible  $\alpha$ -hydrogen atoms.

Another interesting feature that has been observed in the electron-impact fragmentations of the enamine diones is the relative abundance of the molecular ions. It has been observed that in adducts 5, 7 and 35, having the E-configuration, the  $M^+$  peaks appear as low-intensity peaks as compared to the cases of adducts like 6, 8 and 11, having the Z-configuration. In addition, the ready elimination of a phenyl group has been observed in the Z-isomers. It is reasonable to assume, on the basis of these observations, that the Z-isomers may be undergoing a pericyclic reaction under electron-impact, analogous to the transformation of cis-dibenzoylstilbene to give the corresponding lactone derivatives (52). These lactones can subsequently lose a phenyl group, in each case, to

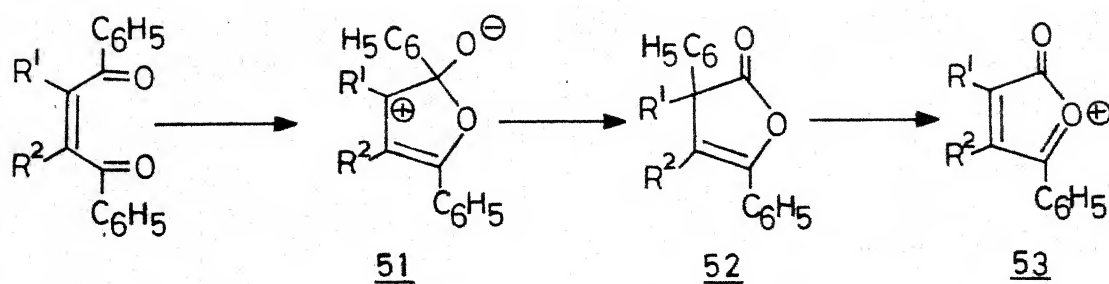




Scheme III.27





Scheme III.28



	<u>R<sup>1</sup></u>	<u>R<sup>2</sup></u>
<u>5</u>	H	HN-C <sub>6</sub> H <sub>5</sub>
<u>6</u>	H	
<u>7</u>	H	HN-C <sub>6</sub> H <sub>4</sub> -OH(o)
<u>8</u>	H	H <sub>5</sub> C <sub>6</sub> -N   CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
<u>11</u>	$R_1R_2=H_5C_6-N\langle=C-C_6H_5$	
<u>35</u>	H	HN- 
<u>50</u>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>

give stable ions like 53 (Scheme III.28).

$\alpha$ -Cleavage of the benzoyl function has been found to be an important fragmentation pathway in both E- and Z-isomers, giving rise to fragments like  $(M-C_6H_5CO)^+$ ,  $C_6H_5CO^+$  and  $C_6H_5^+$  ions.

#### III.4 EXPERIMENTAL

All melting points are uncorrected and were recorded on a Mel-Temp melting point apparatus. The ir spectra were recorded on Perkin-Elmer, Model 137 and Model 521 Infrared Spectrometers. The electronic spectra were recorded on a Beckman DU Spectrophotometer. Nmr traces were recorded on either Varian A-60 or XL-100 Nmr Spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 Mass Spectrometer at 70 eV.

##### III.4.1 Starting Materials

Dibenzoylacetylene, mp 110-111°, was prepared by a reported procedure.<sup>52</sup>

Commercial grades of aniline, piperidine and N-phenylbenzylamine were freshly distilled before use. Nickel peroxide (20 g) was prepared by the treatment of nickel sulphate (40 g) with a mixture of sodium hypochlorite (6% solution, 100 ml) and sodium hydroxide (13 g) as per a reported procedure.<sup>53</sup> Petroleum ether used was of bp 60-80°.

Phenacyl Bromide<sup>54</sup> - Phenacyl bromide, mp 48-49° was prepared in a 85% yield, by the bromination of acetophenone in diethyl ether.

Phenacylaniline<sup>55</sup> - A solution of phenacyl bromide (10 g, 0.05 mol) in ethanol (40 ml) was treated with freshly distilled aniline (10 g, 0.1 mol) and the mixture was gently warmed, during which period a yellow solid precipitated out. The solid material was filtered and recrystallized from alcohol to give 7.2 g (69%) of N-phenacylaniline, mp 98° (lit.<sup>55</sup> mp 98°).

Ir spectrum (KBr)  $\nu_{\max}$ : 3401  $\text{cm}^{-1}$  ( $\nu_{\text{NH}}$ ), 3058, 2841, and 2770  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ); 1689  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); 1603, 1572 and 1504  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

#### III.4.2 Reaction of Aniline with Dibenzoylacetylene

A solution of dibenzoylacetylene (234 mg, 1 mmol) in tetrahydrofuran (10 ml) was added to a tetrahydrofuran solution of aniline (93 mg, 1 mmol in 50 ml) at room temperature and with constant stirring, over a period of 30 minutes. The stirring was continued for an additional period of 30 minutes and afterwards the solvent was removed under vacuum to give a yellow solid. Recrystallization from a mixture (2:1) of methanol and chloroform gave 290 mg (89%) of bright yellow, needle shaped crystals of 1,4-diphenyl-2-(N-phenylamino)but-2-ene-1,4-dione (5), mp 130° (lit.<sup>17</sup> mp 131°).

Anal. Calcd for  $C_{22}H_{17}NO_2$ : C, 80.73; H, 5.19; N, 4.13; Mol. wt., 327. Found: C, 80.58; H, 5.03; N, 3.80; Mol. wt., 327 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{max}$ :  $3120\text{ cm}^{-1}$  ( $\nu_{N-H}$ , hydrogen-bonded),  $3095$ ,  $2945$ ,  $2845\text{ cm}^{-1}$  ( $\nu_{C-H}$ ),  $1670$  and  $1615\text{ cm}^{-1}$  ( $\nu_{C=O}$ ),  $1600$ ,  $1580$  and  $1570\text{ cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Ethanol)  $\lambda_{max}$ :  $258\text{ nm}$  ( $\epsilon$ , 22,600) and  $375$  (19,000).

#### III.4.3 Reaction of Piperidine with Dibenzoylacetylene

A solution of dibenzoylacetylene (936 mg, 4 mmol) in tetrahydrofuran (15 ml) was added to a tetrahydrofuran-solution of piperidine (340 mg, 4 mmol in 80 ml) at room temperature and with constant stirring. After 1 hr, the stirring was stopped and the solvent was removed under vacuum. The residue was recrystallized from a mixture (2:1) of methanol and chloroform to give 1.25 g (98%) of pale yellow needles of 1,4-diphenyl-2-piperidinobut-2-ene-1,4-dione, (6) mp  $179^\circ$  (lit.<sup>17</sup> mp  $181^\circ$ ).

Anal. Calcd for  $C_{21}H_{21}NO_2$ : C, 78.99; H, 6.58; N, 4.39; Mol. wt., 319. Found: C, 78.50; H, 6.49; N, 4.29; Mol. wt., 319 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{max}$ :  $3031$ ,  $3020$ ,  $2956$  and  $2876\text{ cm}^{-1}$  ( $\nu_{C-H}$ ),  $2926$  and  $2855\text{ cm}^{-1}$  ( $\nu_{CH_2}$ , asymmetric and symmetric),  $1670\text{ cm}^{-1}$  ( $\nu_{C=O}$ ),  $1612$ ,  $1599$  and  $1585\text{ cm}^{-1}$  ( $\nu_{C=C}$ )

Uv spectrum (Methanol)  $\lambda_{\max}$ : 255 nm ( $\epsilon$ , 22,000) and 350 (20,500).

#### III.4.4 Reaction of N-Phenylbenzylamine with Dibenzoylacetylene

Treatment of a solution of dibenzoylacetylene (500 mg, 2.1 mmol) in tetrahydrofuran (10 ml) with a tetrahydrofuran-solution of N-phenylbenzylamine (554 mg, 2.1 mmol in 80 ml) at room temperature for 1 hr and work-up of the mixture as in the earlier cases gave a product mixture. Recrystallization of this product from a mixture (2:1) of methanol and chloroform gave 850 mg (81%) of colourless needle shaped crystals of 1,4-diphenyl-2-(N-phenylbenzylamino)-but-2-ene-1,4-dione, (8), mp 133°.

Anal. Calcd for  $C_{29}H_{23}NO_2$ : C, 83.45; H, 5.51; N, 3.36; Mol. wt., 417. Found: C, 83.45; H, 5.41; N, 3.50; Mol. wt., 417 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3016 and 2996  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 1674  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1625, 1599 and 1584  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 258 nm ( $\epsilon$ , 22,000) and 347 (18,600).

#### III.4.5 Reaction of o-Aminophenol with Dibenzoylacetylene

A solution of dibenzoylacetylene (500 mg, 2.1 mmol) in tetrahydrofuran (10 ml) was gradually added to a tetrahydrofuran-solution of o-aminophenol (229 mg, 2.1 mmol in

60 ml), at room temperature, over a period of one hour. The reaction mixture was stirred continuously during the addition. Removal of the solvent under vacuum gave an impure product, which was treated with animal charcoal and subsequently recrystallized from a mixture (1:1) of petroleum ether and chloroform to give 560 mg (77%) of 2-(N-2-hydroxyphenylamino)-1,4-diphenylbut-2-ene-1,4-dione, (7), mp 184-185°.

Anal. Calcd for  $C_{22}H_{17}NO_3$ : C, 76.96; H, 4.95; N, 4.08; Mol. wt., 343. Found: C, 76.88; H, 4.86; N, 4.10; Mol. wt., 343 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3170  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ , hydrogen-bonded), 3070  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1625  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1620, 1605 and 1584  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 260 nm ( $\epsilon$ , 15,000) and 392 (27,000).

#### III.4.6 Reaction of N-Phenacylaniline with Dibenzoylacetylene

A mixture of dibenzoylacetylene (702 mg, 3 mmol) and N-phenacylaniline (633 mg, 3 mmol) in tetrahydrofuran (80 ml) was refluxed for 3 hr on a steam-bath. Removal of the solvent under vacuum gave an oily mass which solidified on treatment with a small amount of methanol. Recrystallization of this product from a mixture (5:1) of petroleum ether and chloroform gave 1 g (78%) of 2,3-dibenzoyl-1,4-diphenylpyrrole, (11), mp 110°.

Anal. Calcd for  $C_{30}H_{21}NO_2$ : C, 83.83; H, 4.91; N, 3.27; Mol. wt., 427. Found: C, 83.52; H, 4.89; N, 3.13; Mol. wt., 427 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 2993, 2987 and 2985  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1655  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1635, 1605, and 1584  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 258 nm ( $\epsilon$ , 26,000) and 326 (6,600).

#### III.4.7 Reaction of *o*-Phenylenediamine with Dibenzoylacetylene

A solution of dibenzoylacetylene (1.17 g, 5 mmol) in tetrahydrofuran (20 ml) was added dropwise to a solution of *o*-phenylenediamine (0.54 g, 5 mmol) in tetrahydrofuran (100 ml) at room temperature over a period of 1 hr, with constant stirring. Removal of the solvent under vacuum gave an orange residue which was recrystallized from a mixture (1:2) of chloroform and methanol to give 1.3 g (80%) of bright orange needles of 2-(2-hydroxy-2-phenylethene)-3-phenylquinoxaline, (22), mp 169°, (lit.<sup>37</sup> mp 169-171°).

Anal. Calcd for  $C_{22}H_{16}N_2O$ : C, 81.48; H, 4.94; N, 8.64; Mol. wt., 324. Found: C, 81.68; H, 5.36; N, 9.1; Mol. wt., 324 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3027 and 3012  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ); 1585 and 1525  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Ethanol)  $\lambda_{\max}$ : 235 nm ( $\epsilon$ , 38,000), 295 (15,000), 335 (15,800) and 432 (17,700).

### III.4.8 Oxidation of 2-(2-Hydroxy-2-phenyletheno)-3-phenyl-quinoxaline with Nickel Peroxide

A solution of 2-(2-hydroxy-2-phenyletheno)-3-phenyl-quinoxaline (500 mg, 2.1 mmol) in benzene (80 ml) was stirred with 3 g of nickel peroxide for 8 hr at room temperature. Filtration of the inorganic material and removal of the solvent under vacuum gave a yellow viscous material which was triturated with methanol to give a yellow solid. Recrystallization of this product from a mixture (1:2) of chloroform and methanol gave 190 mg (38%) of 1,4-diphenyl-2,3-bis(3-phenylquinox-2-yl)-1,4-butanedione, (26), mp 228°.

Anal. Calcd for  $C_{44}H_{30}N_4O_2$ : C, 81.73; H, 4.64; N, 8.67; Mol. wt., 646. Found: C, 82.13; H, 4.75; N, 8.42; Mol. wt. 646 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3066, 2930 and 2865  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 1676  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1586 and 1571  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Chloroform)  $\lambda_{\max}$ : 252 nm ( $\epsilon$ , 60,000) and 336 (17,000).

### III.4.9 Bromination of 2-(2-Hydroxy-2-phenyletheno)-3-phenyl-quinoxaline

To a solution of 2-(2-hydroxy-2-phenyletheno)-3-phenyl-quinoxaline (324 mg, 1 mmol) in carbon tetrachloride (30 ml), was added a carbon tetrachloride-solution of bromine (160 mg, 1 mmol in 20 ml), over a period of 30 minutes and with constant stirring. A solid material



precipitated out during the reaction, which was filtered off and recrystallized from a mixture (2:1) of petroleum ether and chloroform to give 316 mg (97.5%) of 2-bromo-phenacyl-3-phenylquinoxaline (23), mp 185-186°.

Anal. Calcd for  $C_{22}H_{15}N_2OBr$ : C, 65.51; H, 3.72; N, 6.94; Mol. wt., 402. Found: C, 65.69; H, 4.01; N, 7.12; Mol. wt., 402 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$ : 3090, 3055, 3035 and 2955  $\text{cm}^{-1}$  ( $\nu_{C-H}$ ), 1710  $\text{cm}^{-1}$  ( $\nu_{C=O}$ ), 1612, 1595 and 1578  $\text{cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$ : 247 nm ( $\epsilon$ , 29,500) and 332 (6,300).

#### III.4.10 Reaction of 1,8-Diaminonaphthalene with Dibenzoylacetylene

A solution of dibenzoylacetylene (1.17 g, 5 mmol) in tetrahydrofuran (20 ml) was added to a tetrahydrofuran solution of 1,8-diaminonaphthalene (0.79 g, 5 mmol in 100 ml), at room temperature over a period of 1 hr. Removal of the solvent under vacuum gave a product which was chromatographed over silica-gel.

Elution of the column with a mixture (5:1) of petroleum ether and benzene gave a violet compound which was recrystallized from hot chloroform to give 1.15 g (86%) of 2-benzoylperimidine (33), mp 203-204°.

Anal. Calcd for  $C_{18}H_{12}N_2O$  : C, 79.41; H, 4.41; N, 10.29; Mol. wt., 272. Found: C, 79.59; H, 4.70; N, 10.10; Mol. wt., 272 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$  :  $3360\text{ cm}^{-1}$  ( $\nu_{N-H}$ ), 3065, 2946 and  $2866\text{ cm}^{-1}$  ( $\nu_{C-H}$ ),  $1658\text{ cm}^{-1}$  ( $\nu_{C=O}$ ); 1624, 1590 and  $1520\text{ cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$  : 237 nm ( $\epsilon$ , 23,000), 260 (18,000), 285 (14,000), 338 (10,000) and 508 (1,100).

Further elution of the silica-gel column with a mixture (4:1) of petroleum ether and benzene gave 230 mg of a mixture of products which was rechromatographed over silica-gel. Elution with a mixture (5:1) of petroleum ether gave 50 mg of 2-benzoylperimidine, mp  $203-204^\circ$  (mixture mp).

Further elution of the column with a mixture (4:1) of petroleum ether and benzene gave 180 mg (9%) of yellow needle shaped crystals of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine, (32), mp  $146-147^\circ$ .

Anal. Calcd for  $C_{26}H_{20}N_2O_2$  : C, 79.59; H, 5.10; N, 7.14; Mol. wt., 392. Found: C, 79.32; H, 5.42; N, 7.29; Mol. wt., 392 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$  :  $3276\text{ cm}^{-1}$  ( $\nu_{N-H}$ , hydrogen-bonded), 3065 and  $2926\text{ cm}^{-1}$  ( $\nu_{C-H}$ ),  $1650\text{ cm}^{-1}$  ( $\nu_{C=O}$ ), 1638, 1610 and  $1593\text{ cm}^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$  : 235 nm ( $\epsilon$ , 52,500)  
and 335 (17,000).

III.4.11 Thermolysis of 2-Benzoyl-2-phenacyl-2,3-dihydroperimidine

A sample of 2-benzoyl-2-phenacyl-2,3-dihydroperimidine (60 mg, 0.15 mmol) was heated for 30 minutes around 150-155° in a sealed tube. The reaction mixture was chromatographed over silica-gel. Elution with a mixture (5:1) of petroleum ether and benzene gave 30 mg (73%) of 2-benzoylperimidine, mp 203-204° (mixture mp).

Further elution of the column with the same solvent mixture gave 15 mg (25%) of the unchanged starting material, mp 146-147° (mixture mp).

III.4.12 Reaction of 2-Aminopyridine with Dibenzoylacetylene

To a solution of dibenzoylacetylene (2.34 g, 0.01 mol) in ether (300 ml), was added an ether solution of 2-aminopyridine (0.94 g, 0.01 mol in 80 ml) with constant stirring over a period of 45 minutes. On leaving the reaction mixture overnight, a deep red solid compound separated out, which was recrystallized from hot benzene to give 2g (61%) of 2-(2-imino-1(2H)pyridyl)-1,4-diphenylbut-2-ene-1,4-dione (34), mp 168°.

Anal. Calcd for  $C_{21}H_{16}N_2O_2$  : C, 76.82; H, 4.87; N, 8.53; Mol. wt., 328. Found: C, 76.76; H, 5.04; N, 8.45; Mol. wt., 328 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$  : 3115  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ , hydrogen-bonded), 3085 and 3055  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1668 and 1653  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1613, 1588 and 1578  $\text{cm}^{-1}$  ( $\nu_{\text{C=N}}$  and  $\nu_{\text{C=C}}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$  : 260 nm ( $\epsilon$ , 19,500), 295 (15,000) and 452 (7,200).

Removal of the solvent from the mother liquor gave a residual product which was chromatographed over silica-gel. Elution with petroleum ether gave a product which was recrystallized from a mixture (1:1) of benzene and methanol to give 400 mg (12%) of yellow crystals of 1,4-diphenyl-2-(N-2-pyridylamino)but-2-ene-1,4-dione, (35), mp 165°.

Anal. Calcd for  $C_{21}H_{16}N_2O_2$  : C, 76.82; H, 4.87; N, 8.53; Mol. wt., 328. Found: C, 76.90; H, 4.73; N, 8.66; Mol. wt., 328 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{\max}$  : 3160  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ , hydrogen-bonded), 3100 and 3060  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1710  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1630  $\text{cm}^{-1}$  ( $\nu_{\text{C=N}}$ ), 1600, 1580, 1530  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).

Uv spectrum (Methanol)  $\lambda_{\max}$  : 258 nm ( $\epsilon$ , 22,000) and 380 (29,000).

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CHAPTER IV  
THERMAL AND PHOTOCHEMICAL TRANSFORMATIONS  
OF TETRAPHENYL-p-DIOXIN AND  
TETRAPHENYL-p-DITHIIN<sup>1</sup>

IV.1 ABSTRACT

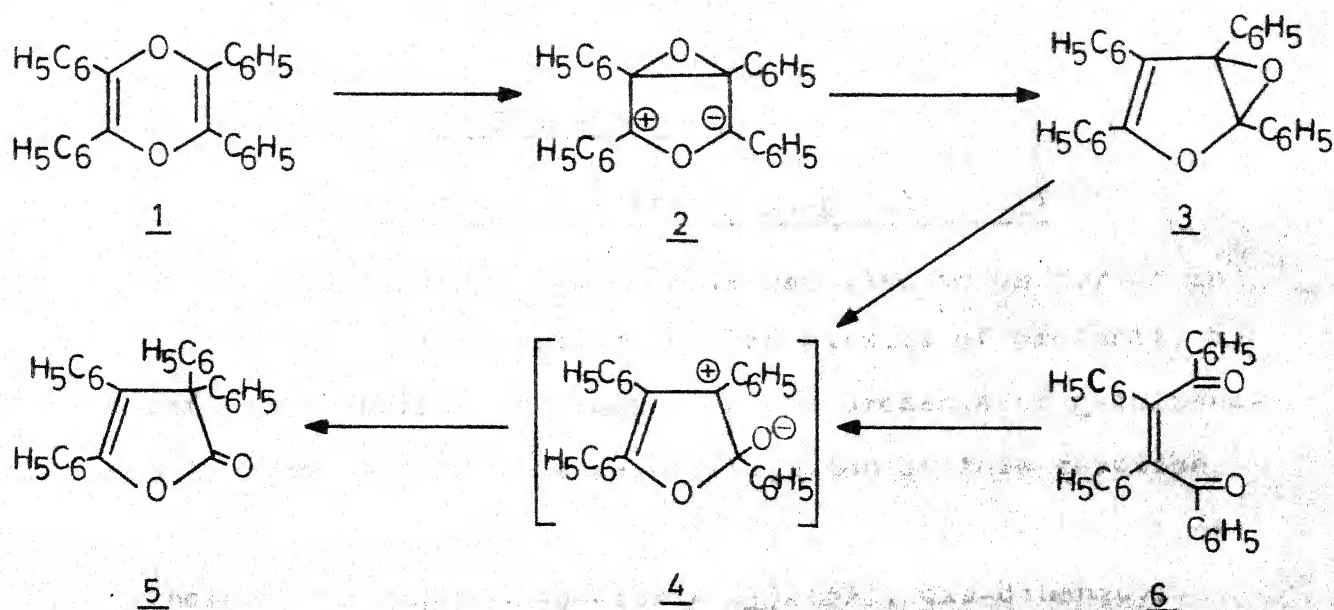
The thermal transformation of tetraphenyl-p-dioxin (1) to 2,2,3,4-tetraphenylbut-3-enolide (5) has been shown to proceed through the intermediacy of cis-dibenzoylstilbene (6) and a reasonable mechanism for this transformation has been suggested. The photolysis of tetraphenyl-p-dioxin, on the other hand, has been found to give a mixture of products consisting of mainly benzil and small amounts of tolan. Thermolysis and photolysis of tetraphenyl-p-dithiin (35) follow a different pathway giving rise to tetraphenylthiophene, in each case.

## IV.2 INTRODUCTION

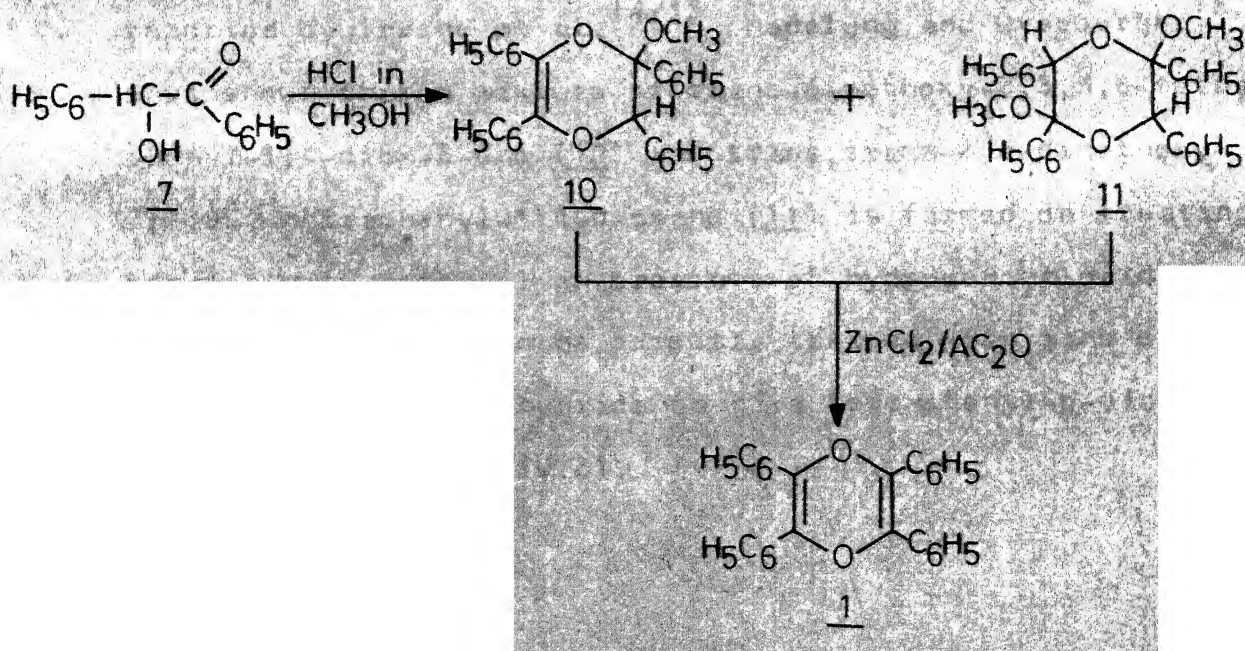
Six-membered heterocycles like p-dioxin and p-dithiin, containing two hetero atoms and of the category of eight-electron systems have received considerable attention in recent years.<sup>2-6</sup> Detailed studies of the uv-spectrum, measurement of bond lengths by electron diffraction method<sup>7</sup> and theoretical calculations,<sup>8</sup> have shown that p-dioxin has a nearly planar structure and that the structural features are favourable for electron delocalization in this system. In contrast, p-dithiin has been shown to have a non-planar boat configuration.<sup>9</sup>

Egger and Summerbell<sup>10</sup> have shown that 2,3,5,6-tetraphenyl-p-dioxin (1) on heating at 250° is converted to 2,2,3,4-tetraphenylbut-3-enolide (5). These workers have rationalized their observation in terms of an initial intermediate 2, which is then transformed to the product 5, through the furan epoxide, 3 and the dipolar intermediate, 4 as shown in Scheme IV.1. The thermal transformation of cis-dibenzoylstilbene (6) is known to give the same lactone 5, formed from tetraphenyl-p-dioxin and the involvement of the dipolar intermediate 4, has been suggested by earlier workers.<sup>11,12</sup> In view of our general interest in the thermal and photochemical transformations of cis-1,2-dibenzoylalkenes, we have examined the thermal and photochemical transformations of both tetraphenyl-p-dioxin and

Scheme IV.1



Scheme IV.2



tetraphenyl-p-dithiin, with a view to understanding the details of these transformations.

#### IV.3 RESULTS AND DISCUSSION

##### IV.3.1 Preparation of Tetraphenyl-p-dioxin (1)

Tetraphenyl-p-dioxin is reported to be formed in poor yields, along with a complex mixture of products, by refluxing benzoin in ligroin in the presence of p-toluene-sulphonic acid.<sup>9</sup> In a reinvestigation of this reaction, Jemmis<sup>13</sup> has shown that the products formed in this case include, tetraphenyl-p-dioxin (1) (6%), cis-dibenzoyl-stilbene (6) (0.5%), benzil (8) (47%), desoxybenzoin (8%) and tetraphenylfuran (9) (12%). A convenient method for preparing tetraphenyl-p-dioxin is through the reaction of benzoin with methanol in presence of hydrogen chloride, as reported by Irvine et al.<sup>14,15</sup> Madelung and Overberger<sup>16,17</sup> have shown that a mixture of trans-6-methoxy-2,3,5,6-tetraphenyl-1,4-diox-2-ene (10) and trans,trans-2,5-dimethoxy-2,3,5,6-tetraphenyl-1,4-dioxane (11) is formed on treating benzoin with methanol in presence of hydrogen chloride and that this mixture can be directly treated with zinc chloride in boiling acetic anhydride to give tetraphenyl-p-dioxin in good yields (Scheme IV.2).

#### IV.3.2 Thermolysis of Tetraphenyl-p-dioxin

Although the thermolysis of tetraphenyl-p-dioxin (1) in the absence of any solvent at 250° has been reported to give exclusively the lactone 5 in a 90% yield,<sup>10</sup> we have found in our present studies that actually a mixture of products consisting of both the lactone 5 (84%) and cis-dibenzoylstilbene (6, 10%) is formed on neat heating of 1 at 260° for 45 minutes. When the thermolysis of 1, however, was conducted at lower temperatures and in different solvents under reflux, an increase in the yield of cis-dibenzoylstilbene has been observed. In refluxing toluene (110°) for example, a 10% yield of benzil (8) was obtained after 45 hr and most of the starting material (81%) was recovered unchanged. In refluxing o-dichlorobenzene (180°), on the other hand, 1 gave mainly cis-dibenzoylstilbene. Small amounts of benzil were also formed in all these cases. When 1 was refluxed in nitrobenzene (210°) for 20 hr, a 91% yield of the lactone 5 and a 8% yield of cis-dibenzoylstilbene were formed. Table IV.1 summarizes the results of these studies.

The results of our studies clearly show that under thermal conditions, tetraphenyl-p-dioxin (1) is first converted to cis-dibenzoylstilbene (6), which then at higher temperatures is transformed to 2,2,3,4-tetraphenylbut-3-enolide (5). The transformation of 1 to 5, in principle,

Table IV.1 - Thermolysis of Tetraphenyl-p-dioxin (1) at Different Temperatures

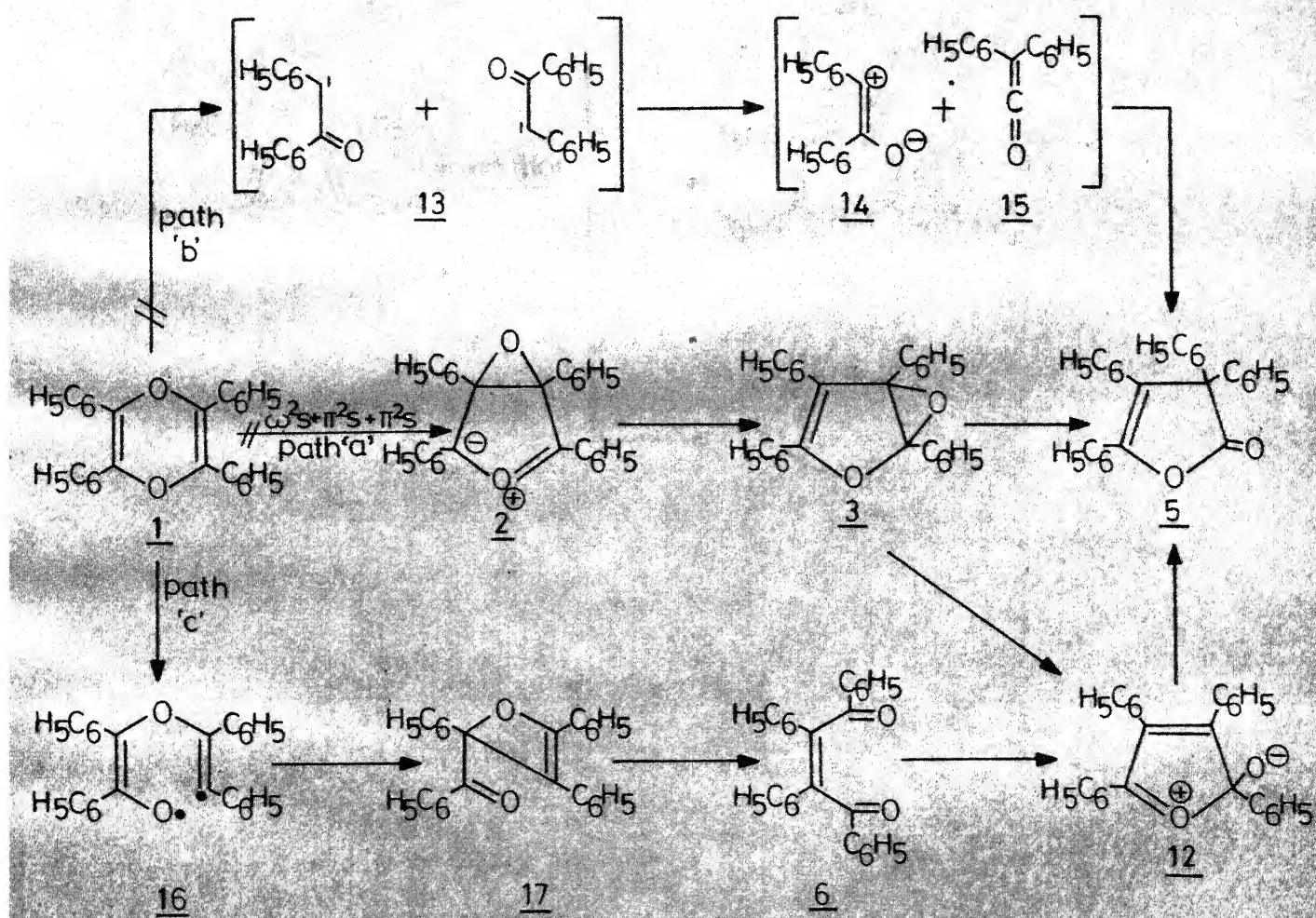
Solvent	Temperature (°C)	Time (hr)	Recovered <u>1</u>	Products (%)		
				<u>5</u>	<u>6</u>	<u>8</u> *
Toluene	110	45	81	-	-	10
<u>o</u> -Dichloro-benzene	180	38	8	-	82	16
<u>o</u> -Dichloro-benzene	180	45	5	-	81	24
<u>o</u> -Dichloro-benzene	180	50	-	3	79	30
Nitrobenzene	210	20	-	91	8	-
No solvent	260	$\frac{3}{4}$	-	84	10	-

\*Formed by the air-oxidation of 1.

can proceed through different pathways as shown in Scheme IV.3. One of these routes (Path 'a') would involve an initial electrocyclic reaction of 1 through a  $[\omega^2s+\pi^2s+\pi^2s]$  type of reaction to form the carbonyl ylid 2, which can subsequently undergo transformation to the furan epoxide, 3. Subsequent conversion of 3 to the lactone 5 can take place either through a dyotropic rearrangement or in a stepwise process involving the zwitterionic intermediate 10. The fact that cis-dibenzoylstilbene (6) is formed as an intermediate in the transformation of 1 to 5 would preclude this pathway. However, with a view to ascertaining whether the furan epoxide 3 is formed as an intermediate in the transformation of 1 to 5, we have attempted at preparing this epoxide through the peracid oxidation of tetraphenylfuran. It is known that tetraphenylfuran (9) undergoes peroxidation under varying experimental conditions to give different products like cis-dibenzoylstilbene (6), the enol benzoate of dibenzoylphenylmethane (18) and cis-dibenzoylstilbene epoxide (19), as shown in Scheme IV.4.<sup>18</sup> In the present studies we find that the oxidation of 1 employing an equimolar amount of perbenzoic acid gives a nearly quantitative yield of cis-dibenzoylstilbene. Our efforts at isolating the furan epoxide intermediate 3, even at low temperatures have been unsuccessful.

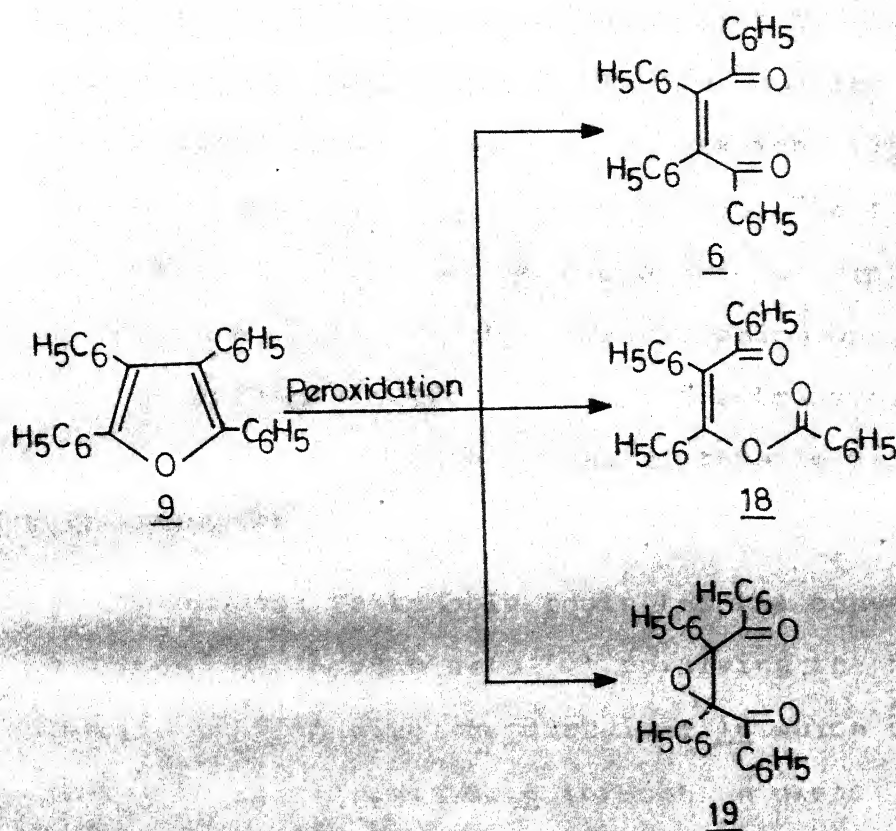


Scheme IV.3

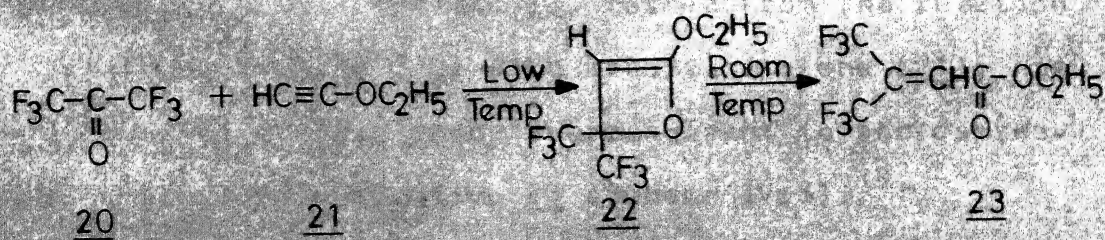




Scheme IV.4



Scheme IV.5



An alternative mode of transformation of 1 would be through path 'b', involving the initial formation of the ketocarbene 13. This ketocarbene intermediate, which can exist in the 1,3-dipolar form 14, can undergo a subsequent cycloaddition reaction with diphenylketene (15), formed by the rearrangement of 13 (Scheme IV.3). The fact that the ketocarbene intermediate 13 could not be trapped by dipolarophiles like dimethyl acetylenedicarboxylate and also the intramolecular nature of the transformation of 1 to 5 would rule out path 'b' as a probable pathway for this transformation.

The most reasonable route for the conversion of 1 to 5 seems to be through path 'c' involving the homolytic cleavage of 1 to give the diradical 16 which can subsequently be transformed to 6 through an oxete intermediate 17. Electrocyclic ring-closure of 6 would give rise to the zwitterionic intermediate 12, which is rearranged to 5 (Scheme IV.3). In this connection, it may be mentioned that the oxete intermediate 22, formed from the reaction of hexafluoroacetone (20) with ethoxyacetylene (21), has been shown to undergo ready rearrangement to the corresponding ethylene derivative 23 (Scheme IV.5).<sup>19</sup>

It has been observed that benzil is formed as a minor product in the thermolysis of 1 and that the yields of benzil increases with increased duration of heating.

A reasonable pathway for the formation of benzil in this reaction is through the partial air-oxidation of 1, under thermolytic conditions. The fact that benzil is formed in nearly quantitative yield on treatment of 1 with peracids would support this assumption.

#### IV.3.3 Photolysis of Tetraphenyl-p-dioxin (1)

In the thermolysis of 1, if a diradical intermediate like 16 (Scheme IV.3) is involved, its formation should be more prominent under photochemical conditions. With a view to examining this possibility we have studied the photolysis of 1 under different conditions.

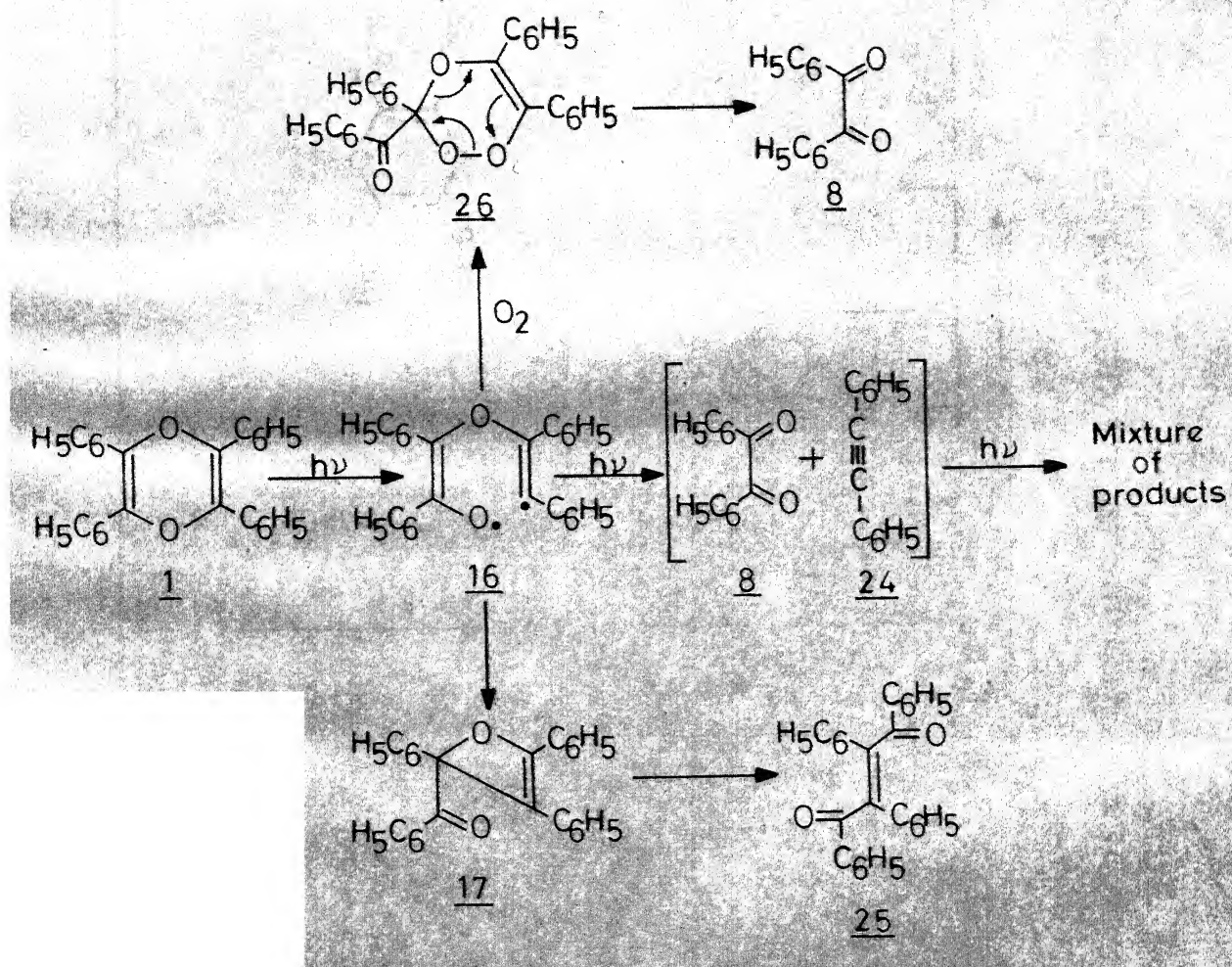
Photolysis of 1 in t-butanol for 15 minutes gave a 56% yield of benzil (8) and 4% yield of tolan (24), besides a 33% of the unchanged starting material. When the photolysis was carried out in benzene for 2 1/2 hr, under nitrogen atmosphere, a mixture of products consisting of benzil (30%), tolan (1%) and trans-dibenzoylstilbene (25, 1.7%) was obtained, besides 53% of the starting material. When the photolysis, however, was carried out in the presence of air, a 70% yield of benzil was obtained besides 20% of the unchanged starting material. The photolysis of 1 in benzene for 10 minutes under oxygen atmosphere gave a 60% yield of benzil. However, when the time of irradiation was increased to 30 minutes, besides a 6% yield of benzil,

a complex mixture of products was obtained from which no definite product could be isolated. Examination of this mixture on tlc showed that it closely resembles the products obtained from the photolysis of benzil<sup>20</sup> and tolan.<sup>21</sup>

From the results of our studies it appears that under photochemical conditions 1 undergoes homolytic cleavage to give the diradical intermediate 16, which subsequently undergoes either fragmentation to give benzil (8) and tolan (24), or air-oxidation to give benzil via a peroxy intermediate like 26. Both benzil and tolan, under photochemical conditions would undergo further transformations to give the complex mixture of products (Scheme IV.6). The formation of small amounts of trans-dibenzoylstilbene (25) in the photolysis of 1 in benzene would suggest that a small fraction of 16 may be getting converted to 17 and subsequently to 25 under these conditions.

In continuation to our studies we have examined the electron-impact fragmentation of tetraphenyl-*p*-dioxin. The mass spectrum of 1 (Fig. IV.1) showed the molecular ion peak at m/e 388 (16). Other peaks in the spectrum were observed at m/e 311 (1), 283 (3), 267 (1), 255 (4), 179 (5), 178 (31), 177 (3), 176 (6), 165 (3), 152 (5), 151 (4), 105 (100), 77 (35), 71 (6), 70 (4), 69 (6), 57 (11), 56 (3), 55 (10), 51 (6), 43 (10) and 41 (6). A comparison

Scheme IV.6



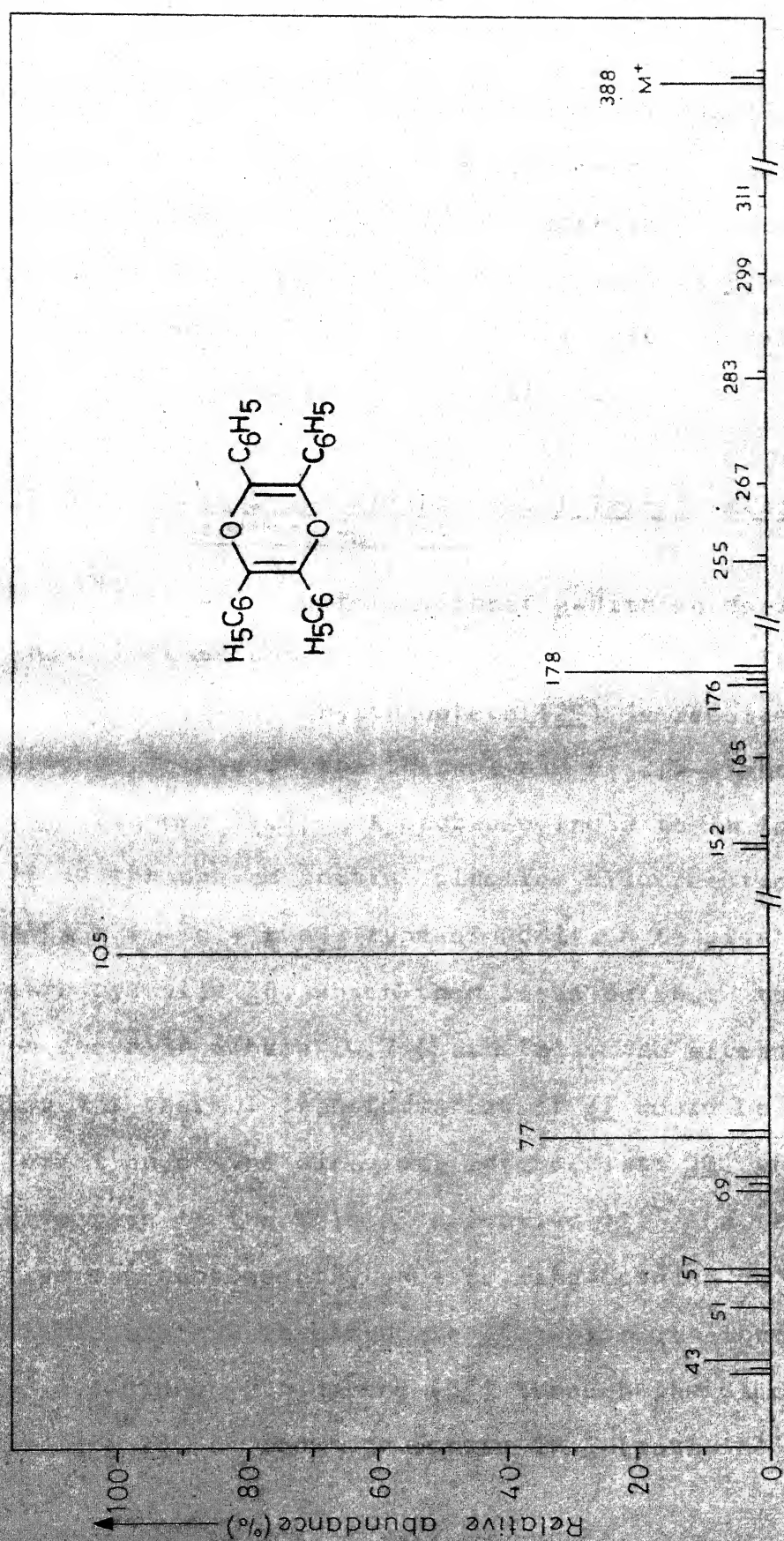


Fig. IV.1 Mass spectrum of tetraphenyl-p-dioxin (1)

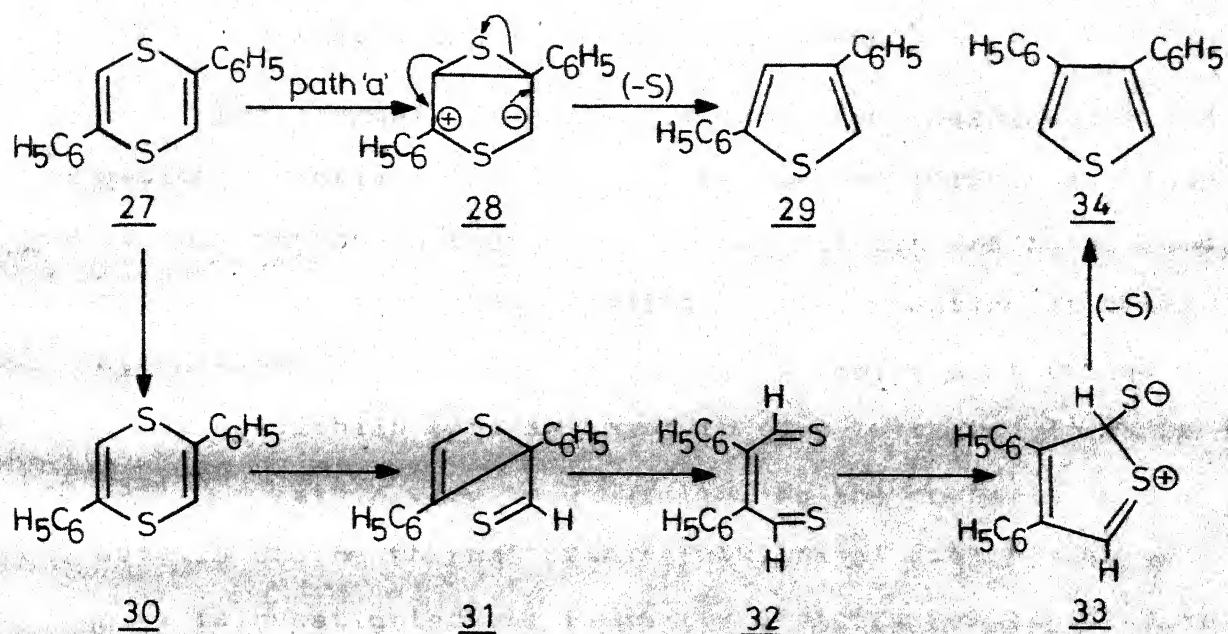


of the mass spectrum of 1 with that of cis-dibenzoylstilbene (6) (see, Chapter I, Scheme I.8) reveals a striking similarity between the two, which essentially indicates that 1, upon electron impact is transformed to 6, which subsequently undergoes fragmentation to give different ions, as shown in Scheme I.8 (Chapter I).

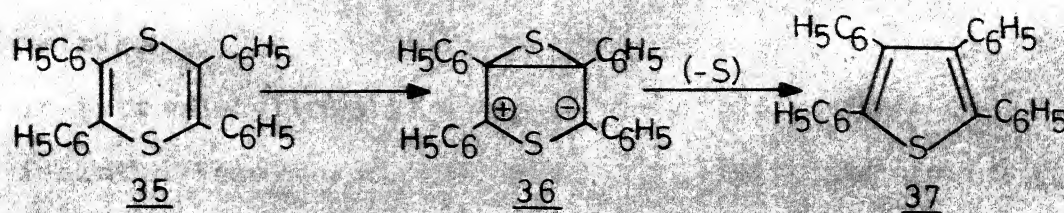
#### IV.3.4 Thermal and Photochemical Transformations of Tetraphenyl-p-dithiin

Thermal transformations of p-dithiin derivatives are known to give substituted thiophenes.<sup>22-24</sup> Thus, for example, 2,3-diphenylthiophene (29) is reported to be the product formed in the thermolysis of 2,5-diphenyl-p-dithiin (27) (Scheme IV.7). A probable route to the formation of 29 is through an initial electrocyclic reaction of 27 by a  $[\omega^2s + \pi^2s + \pi^2s]$  type of addition to give the thio-carbonyl ylid 28, which then loses sulphur to give 29, as shown in Scheme IV.7 (path 'a'). An alternative pathway for the thermal transformation of 27 would be through the formation of the diradical intermediate 30, which can then give rise to the thiete derivative 31. The thiete derivative can subsequently undergo ring-opening to give the dithiocarbonyl intermediate 32, which can then give rise to 3,4-diphenylthiophene (34) through the dipolar intermediate 33, as shown in Scheme IV.7 (path 'b'). However,

Scheme IV.7



Scheme IV.8





the exclusive formation of 2,3-diphenylthiophene from 27 and not 3,4-diphenylthiophene (34) would clearly indicate that path 'a' is followed in the thermal transformation of 27. A similar observation has been made in the thermolysis of 2,5-diphenyl-3-nitro-p-dithiin, which gives exclusively 3,5-diphenyl-2-nitrothiophene.<sup>23</sup>

The thermal transformation of a few tetrasubstituted p-dithiin derivatives are reported in the literature. Thus, it has been shown that tetracyano-p-dithiin undergoes ready thermal transformation, leading to the formation of tetracyanothiophene.<sup>25</sup> Similarly, the thermolysis of tetraphenyl-p-dithiin (35) is known to give tetraphenylthiophene (37).<sup>26</sup> With a view to understanding the mechanistic details of the thermal transformations of p-dithiins, we have reinvestigated the reactions of tetraphenyl-p-dithiin (35). The thermolysis of 35 at 195° for 30 minutes and in the absence of any solvent gave rise to a 97% yield of tetraphenylthiophene (37). The same reaction, when carried out in refluxing p-dichlorobenzene, gave a 95% yield of tetraphenylthiophene (37). No other product could be isolated from these reactions. If the formation of 37 is proceeding through the thiocarbonyl ylid intermediate 36, as shown in Scheme IV.8, then its presence could be detected by trapping experiments. Our attempts to trap the intermediate 36 with dipolarophiles like dimethyl

acetylenedicarboxylate have been unsuccessful. It is quite likely that this intermediate undergoes a rapid loss of sulphur to give the thiophene derivative 37 (Scheme IV.8).

Further to our studies, we have examined the photolysis of tetraphenyl-p-dithiin (35). Photolysis of a benzene solution of 35 resulted in a 15% yield of tetraphenylthiophene 37. The formation of 37 in this reaction may be rationalized in terms of a pathway similar to the thermal transformation of 35, as shown in Scheme IV.8 or through a diradical pathway similar to path 'b' in Scheme IV.7. It might be mentioned in this connection that recent studies show that the photooxygenation of tetraphenyl-p-dithiin gives rise to a mixture of products consisting of tetraphenylthiophene (37) (31%), benzil (8) (15%) and benzoic acid (26%).<sup>27</sup>

In the present studies, we have also examined the electron-impact induced fragmentation of tetraphenyl-p-dithiin. The mass spectrum of 35 (Fig. IV.2) showed a molecular ion peak at  $m/e$  420 (76). The most intense peak in the spectrum of 35, however, was observed at  $m/e$  388 (100). Other major peaks in the mass spectrum of 35 were present at  $m/e$  310 (5), 309 (11), 308 (7), 307 (7), 277 (4), 267 (7), 266 (5), 221 (3), 210 (5), 178 (67), 165 (12), 155 (4), 154 (3), 152 (3), 151 (2), 121 (63), 77 (9), 64 (3) and 51 (1). It is pertinent to observe that the mass spectrum of 35 shows great similarity

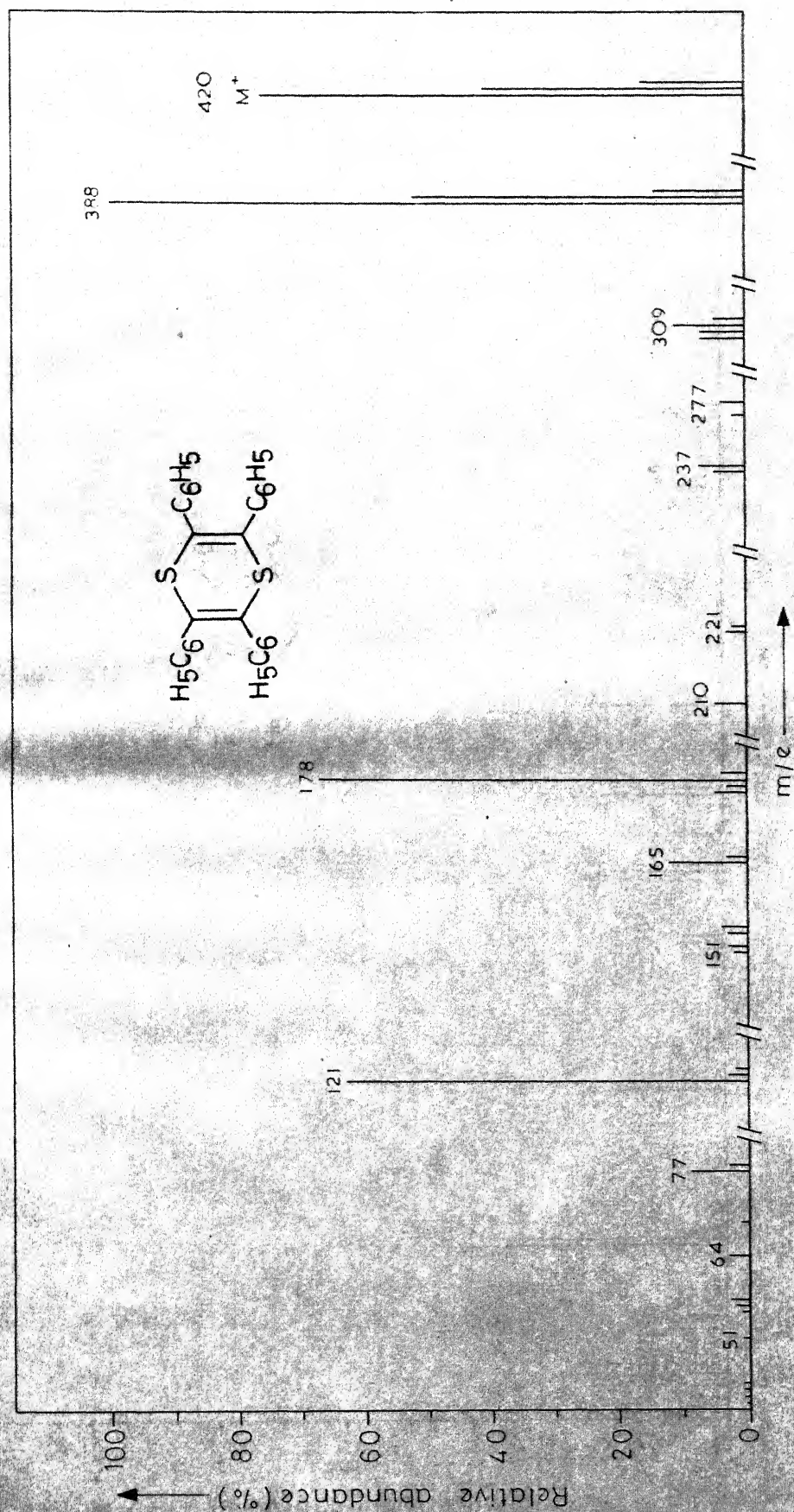


Fig. IV.2 Mass spectrum of tetraphenyl-p-dithiin (41)

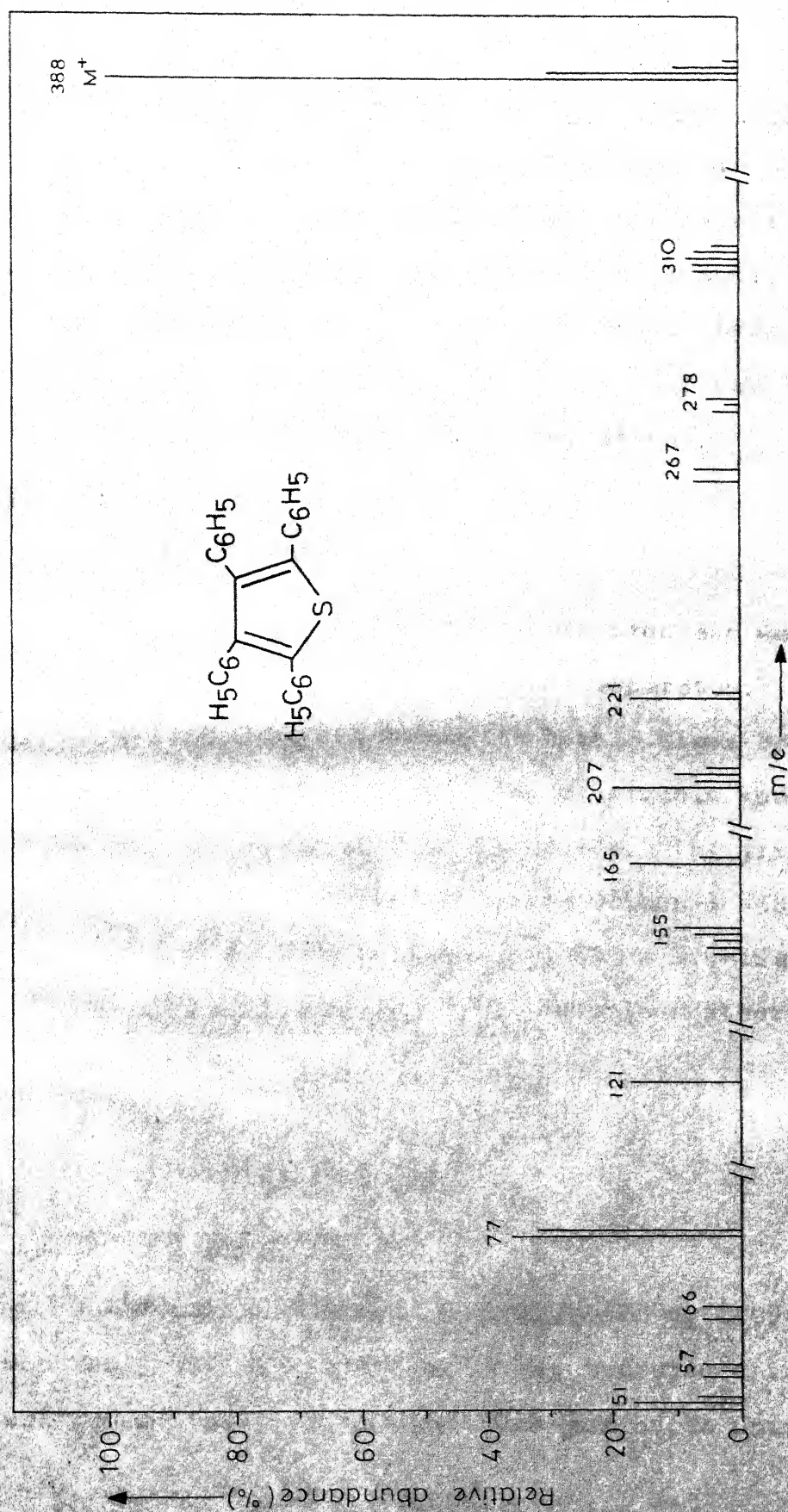


Fig. IV-3 Mass spectrum of tetraphenylthiophene (43)

to that of tetraphenylthiophene (37) (Fig. IV.3),<sup>28</sup> excepting for the presence of the molecular ion peak in 35 at m/e 420. It is apparent from the mass spectrum of 35 that it undergoes ready conversion to tetraphenylthiophene (37), under electron-impact, and in this respect the mass spectral behaviour of 35 is very similar to its thermal and photochemical transformations.

#### IV.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. Infrared spectra were recorded either on Perkin-Elmer Model 137 or 521 Infrared Spectrometers. The electronic spectra were recorded on a Beckman DB Spectrometer. The irradiation experiments were carried out using either a 450 W Hannoveria medium pressure mercury lamp or a 150 W Srinivasan-Griffin Rayonet Photochemical Reactor. Petroleum ether used was of bp 60-80°.

##### IV.4.1 Starting Materials

##### Tetraphenyl-p-Dioxin (1)<sup>17</sup>

Through a solution of benzoin (20 g, 0.094 mol) in methanol (500 ml), a stream of dry hydrogen chloride gas was passed for 1 hr, during which period, a white crystalline

solid separated out. After keeping the reaction mixture at room temperature for 12 hr, the solid material was filtered off to give 7 g of a mixture of products consisting of both trans-6-methoxy-2,3,5,6-tetraphenyl-1,4-diox-2-ene (10) and trans,trans-2,5-dimethoxy-2,3,5,6-tetraphenyl-1,4-dioxane (11). This mixture of products (5 g) was subsequently heated with 75 ml of acetic anhydride and 0.5 g of anhydrous zinc chloride till the solution began to boil. On cooling, a bright yellow solid separated out which gave 4 g (22%) of tetraphenyl-p-dioxin (1) mp 218° (lit.<sup>17</sup> mp 218°), on recrystallization from a mixture (1:1) of chloroform and petroleum ether.

#### Tetraphenylfuran (9)<sup>29</sup>

A mixture of benzoin (2 g, 9.4 mmol) and anhydrous aluminium chloride (30 mg) was heated in an evacuated sealed tube around 150-200° for 50 hr. The reaction mixture was extracted with carbon tetrachloride. Removal of the solvent from the carbon tetrachloride-extract gave a product mixture. Treatment of this mixture with ethanol gave an ethanol-insoluble product, which on recrystallization from a mixture (10:1) of petroleum ether and benzene gave 1.2 g (31%) of tetraphenylfuran (9), mp 173-174° (lit.<sup>29</sup> mp 173°).

Tetraphenyl-p-Dithiin (35)<sup>30</sup>

Benzoin (5 g, 0.023 mol) was added to 100 ml of ethanol which had been saturated previously with dry hydrogen chloride gas. A stream of hydrogen sulphide was passed through this suspension. All of the benzoin gradually went into solution and after passing the gas for 1 hr, a solid material started precipitating out. After allowing the reaction to proceed for 2 hr, the precipitated material was removed by filtration. The filtered solid was treated with hot ethanol to remove the ethanol-soluble impurities and the residue was recrystallized from chloroform to give 5 g (50%) of tetraphenyl-p-dithiin (35), mp 191° (lit.<sup>30</sup> mp 191°).

IV.4.2 Thermolysis of Tetraphenyl-p-dioxinA In Toluene

A sample of tetraphenyl-p-dioxin (300 mg, 0.77mmol) was refluxed in toluene (15 ml) for 45 hr. Removal of the solvent under vacuum gave a product which was extracted with petroleum ether. The residue gave 237 mg (79%) of the unchanged starting material, mp 217-218° (mixture mp), after recrystallization from a mixture (1:1) of chloroform and petroleum ether.

The petroleum ether-extract was chromatographed over an alumina column. Elution of the column with petroleum ether (bp 60-80°) gave an additional 7 mg (2%) of the starting material, mp 217-218° (mixture mp) after recrystallization from a mixture (1:1) of petroleum ether and chloroform.

Further elution of the column with petroleum ether gave 6 mg (10%) of benzil, mp 91° (mixture mp).

#### B In o-Dichlorobenzene

A sample of tetraphenyl-p-dioxin (500 mg, 1.3 mmol) was refluxed in o-dichlorobenzene (25 ml) for 38 hr. The solvent was completely removed under vacuum. The reaction mixture was treated with petroleum ether and the insoluble residue was subsequently treated with hot ethanol. The ethanol-insoluble residue gave 40 mg (8%) of tetraphenyl-p-dioxin, mp 217-218° (mixture mp), after recrystallization from a mixture (1:1) of chloroform and petroleum ether. The ethanol-soluble portions, on cooling gave 335 mg (73%) crystals of cis-dibenzoylstilbene (6), mp 216-217° (mixture mp).

The petroleum ether-soluble portion was chromatographed over an alumina column. Elution of the column with petroleum ether (bp 60-80°) gave 15 mg (16%) of benzil mp 91° (mixture mp).

Further elution of the column with a mixture (3:1) of petroleum ether and benzene gave an additional 40 mg (9%)



of cis-dibenzoylstilbene, mp 216-217° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and benzene.

In a repeat run, tetraphenyl-p-dioxin (500 mg, 1.3 mmol) was refluxed in o-dichlorobenzene (15 ml) for 45 hr. Work-up as in the earlier case gave 25 mg (5%) of the starting material, mp 217-218° (mixture mp), 385 mg (81%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp) and 24 mg (24%) of benzil, mp 91° (mixture mp).

In yet another run, tetraphenyl-p-dioxin (500 mg, 1.3 mmol) was refluxed in o-dichlorobenzene for 50 hr. Work-up in the usual manner gave a total amount of 393 mg (79%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), 30 mg (30%) of benzil, mp 91° (mixture mp) and 15 mg (3%) of 2,2,3,4-tetraphenylbut-3-enolide, mp 136-137° (mixture mp).

#### C     In Nitrobenzene

A sample of tetraphenyl-p-dioxin (500 mg, 1.3 mmol) was refluxed in nitrobenzene (25 ml) for 20 hr. The solvent was removed under reduced pressure and the residue was chromatographed over alumina. Elution of the column with a mixture (5:1) of petroleum ether and benzene gave 455 mg (91%) of 2,2,3,4-tetraphenylbut-3-enolide, mp 136-137° (mixture mp) after recrystallization from a mixture (4:1) of petroleum ether and benzene. Further elution with a

mixture (3:1) of petroleum ether and benzene gave 40 mg (8%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and benzene.

#### D In the Absence of Any Solvent

A sample of tetraphenyl-p-dioxin (776 mg, 2 mmol) was heated around 260° for 45 minutes. The residue was chromatographed over alumina. Elution of the column with a mixture (5:1) of petroleum ether and benzene gave 653 mg (84%) of 2,2,3,4-tetraphenylbut-3-enolide, mp 137° (mixture mp), after recrystallization from a mixture (4:1) of petroleum ether and benzene.

Further elution of the column with a mixture (3:1) of petroleum ether and benzene gave 78 mg (10%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and benzene.

#### IV.4.3 Reaction of Tetraphenylfuran with Perbenzoic Acid

A mixture of tetraphenylfuran (1 g, 2.7 mmol) and perbenzoic acid (3 mmol, 34 ml) in chloroform (30 ml) was kept at room temperature for 24 hr. The reaction mixture was washed repeatedly with a 5% solution of sodium bicarbonate and then with water and subsequently dried over anhydrous

sodium sulphate. Removal of the solvent under reduced pressure gave 1 g (96%) of cis-dibenzoylstilbene, mp 216° (mixture mp), on recrystallization from a mixture (1:1) of petroleum ether and benzene.

The bicarbonate-extract was acidified with 1% hydrochloric acid and was then extracted with ether. Removal of the solvent under vacuum gave 300 mg (92%) of benzoic acid, mp 121° (mixture mp), after recrystallization from hot water.

#### IV.4.4 Attempted Thermolysis of Tetraphenyl-p-dioxin in Presence of Dimethyl Acetylenedicarboxylate (DMAD)

A mixture of tetraphenyl-p-dioxin (200 mg, 0.52 mmol) and dimethyl acetylenedicarboxylate (148 mg, 1.04 mmol) was refluxed in o-dichlorobenzene (15 ml) for 38 hr. Both the solvent and unchanged acetylenic ester were removed under vacuum and the reaction mixture was extracted with petroleum ether. The petroleum ether-insoluble product was extracted with hot ethanol to give 40 mg (8%) of tetraphenyl-p-dioxin, as ethanol-insoluble material, which melted at 217-218° (mixture mp). The ethanol soluble portion, on work-up gave 372 mg (82%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp).

The petroleum ether-extract was chromatographed over alumina. Elution of the column with petroleum ether gave

40 mg (16%) of benzil, mp 91° (mixture mp). Further elution of the column with a mixture (3:1) of petroleum ether and benzene gave an additional crop of cis-dibenzoylstilbene (38 mg, 8%), mp 216-217° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and benzene.

#### IV.4.5 Reaction of Tetraphenyl-p-dioxin with Perbenzoic Acid

A mixture of tetraphenyl-p-dioxin (200 mg, 0.52 mmol) and perbenzoic acid (6.8 ml, 0.52 mmol) in chloroform (15 ml) was kept at room temperature for 1 hr. The reaction mixture was washed several times with a 5% solution of sodium bicarbonate and then with water. Removal of the solvent from the chloroform solution gave a residue which was chromatographed over alumina. Elution with petroleum ether gave 104 mg (93%) of benzil, mp 91° (mixture mp). Further elution of the column with petroleum ether gave 90 mg (45%) of unchanged starting material, mp 217-218° (mixture mp).

In a repeat run, 70 mg (0.18 mmol) of tetraphenyl-p-dioxin and excess of perbenzoic acid (5 ml, 0.38 mmol) in chloroform (10 ml) was kept at room temperature for 1 hr. Work-up of the mixture as in the earlier case gave 72 mg (95%) of benzil, mp 91° (mixture mp), after recrystallization from a mixture (10:1) of petroleum ether and benzene.

#### IV.4.6 Photolysis of Tetraphenyl-p-dioxin

##### A In t-Butanol

A solution of tetraphenyl-p-dioxin (750 mg, 1.95 mmol) in t-butanol (210 ml) was irradiated for 15 minutes under nitrogen atmosphere. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with petroleum ether gave 10 mg (4%) of tolan, mp 61-62° (mixture mp). Further elution with petroleum ether gave 250 mg (33%) of the unchanged starting material, mp 218° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and chloroform. Continued elution of the column with petroleum ether gave 150 mg (56%) of benzil, mp 91° (mixture mp), which was recrystallized from a mixture (10:1) of petroleum ether and benzene.

##### B In Benzene

A solution of tetraphenyl-p-dioxin (600 mg, 1.56 mmol) in dry benzene (700 ml) was photolysed under a dry nitrogen atmosphere for 2½ hr. The photolysis was repeated several times until 1.9 g (4.94 mmol) of the starting material was used up and the combined product mixture was chromatographed over alumina.

Elution of the column with petroleum ether gave 12 mg of a viscous material which was rechromatographed over a

small silica-gel column to give 4 mg (1%) of tolan, mp 61-62° (mixture mp).

Continued elution of the column with petroleum ether gave 1 g (53%) of the unchanged starting material, mp 217-218° (mixture mp), after recrystallization from a mixture (1:1) of petroleum ether and chloroform. Further elution with the same solvent gave 150 mg (30%) of benzil, mp 91° (mixture mp) which was recrystallized from a mixture (10:1) of petroleum ether and benzene.

Subsequent elution of the column with a mixture (20:1) of petroleum ether and benzene gave 15 mg (1.7%) of trans-dibenzoylstilbene mp 239° (mixture mp).

#### C In Presence of Air

A solution of tetraphenyl-p-dioxin (100 mg, 0.26 mmol) was photolysed in dry benzene (210 ml) for 15 minutes. Removal of the solvent gave a product mixture which was chromatographed over alumina. Elution with petroleum ether gave 61 mg (70%) of benzil, mp 91° (mixture mp). Further elution of the column with petroleum ether gave 20 mg (20%) of the unchanged starting material, mp 217-218° (mixture mp).

#### D In Presence of Oxygen

A solution of tetraphenyl-p-dioxin (150 mg, 0.39 mmol) in dry benzene (210 ml) was photolysed for 30 minutes, under

oxygen bubbling. Removal of the solvent gave a product which was chromatographed over alumina. Elution with petroleum ether gave 10 mg (6%) of benzil, mp 91° (mixture mp).

Further elution of the column gave 100 mg of a complex mixture from which no definite compound could be isolated.

In a repeat run, a sample of tetraphenyl-p-dioxin (150 mg, 0.39 mmol) was photolysed for 10 minutes in dry benzene (210 ml) under oxygen bubbling. Work-up of the mixture as in the earlier case gave 90 mg (60%) of benzil mp 91° (mixture mp), after recrystallization from a mixture (10:1) of petroleum ether and benzene. No other product could be isolated from this run.

#### IV.4.7 Photolysis of a Mixture of Benzil and Tolan

A mixture of benzil (105 mg, 0.5 mmol) and tolan (89 mg, 0.5 mmol) was taken in dry benzene (210 ml) and was photolysed for 2½ hr, under nitrogen atmosphere. Thin layer chromatography comparison of this photolysed mixture with the complex mixture obtained from the photolysis of tetraphenyl-p-dioxin under identical conditions, showed similarity in many respects.

#### IV.4.8 Thermolysis of Tetraphenyl-p-dithiin

##### A Without Any Solvent

Tetraphenyl-p-dithiin (100 mg, 0.24 mmol) was heated

in a test tube around 195° for 30 minutes. The reaction product was recrystallized from a mixture (3:1) of petroleum ether and chloroform to give 90 mg (97%) of tetraphenylthiophene, mp 190-191° (lit.<sup>26</sup> mp 184-185°).

Anal. Calcd for  $C_{28}H_{20}S$  : C, 86.5; H, 5.15; Mol. wt., 388. Found: C, 86.94; H, 4.9; Mol. wt., 388 (Mass spectrometry).

Ir spectrum (KBr)  $\nu_{max}$  : 3200 and 2425  $cm^{-1}$  ( $\nu_{C-H}$ ), 1610, 1500 and 1485  $cm^{-1}$  ( $\nu_{C=C}$ ).

Uv spectrum ( $CHCl_3$ )  $\lambda_{max}$  : 245 nm ( $\epsilon$ , 25,100), 255 (20,000) and 315 (16,000).

#### B In *o*-Dichlorobenzene

A solution of tetraphenyl-*p*-dithiin (100 mg, 0.24 mmol) in *o*-dichlorobenzene (10 ml) was refluxed for 4 hr. After removal of the solvent, the residual product was recrystallized from a mixture (3:1) of petroleum ether and chloroform to give 88 mg (95%) of tetraphenylthiophene, mp 190-191° (mixture mp).

#### IV.4.9 Attempted Reaction of Tetraphenyl-*p*-dithiin with Dimethyl Acetylenedicarboxylate

A mixture of tetraphenyl-*p*-dithiin (100 mg, 0.24 mmol) and dimethyl acetylenedicarboxylate (67 mg, 0.47 mmol) was refluxed in *o*-dichlorobenzene (10 ml) for 4 hr.



Removal of the solvent and recrystallisation of the residue from a mixture (3:1) of petroleum ether and chloroform gave 88 mg (95%) of tetraphenylthiophene, mp 190-191° (mixture mp). No other product could be isolated from this run.

#### IV.4.10 Photolysis of Tetraphenyl-p-dithiin

A solution of tetraphenyl-p-dithiin (250 mg, 0.6 mmol) in dioxan (225 ml) was photolysed for 8 hr under nitrogen atmosphere. Removal of the solvent gave a product which was chromatographed over silica gel. Elution with petroleum ether gave 33 mg (15%) of tetraphenylthiophene, mp 190-191° (mixture mp).

Elution of the column with a mixture (4:1) of petroleum ether and benzene gave 15 mg (6%) of the unchanged starting material, mp 190-191° (mixture mp).

IV.5 REFERENCES

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## VITAE

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